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Development of fused phosphate fertilizers

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DEVELOPMENT OF FUSED PHOSPHATE FERTILIZERS

by

David R. Boylan

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SUMMARY

An investigation was undertaken to develop phosphate fertilizers by fusing phosphate rock with (a) langbeinite ($K_2SO_4 \cdot 2MgSO_4$), (b) magnesium or potassium sulfate, (c) mixtures of magnesium and potassium sulfate, and (d) other addition agents. Such fertilizers would have the advantage of containing plant nutrients other than phosphorus, e.g., magnesium and potassium, and would be especially suitable for soils deficient in these elements. In addition, the fused products would be basic and could be immediately bagged and shipped without further curing. The process would require neither critical sulfuric acid nor expensive phosphoric acid, as do the present acidulation processes, and might therefore be well adapted to the Midwest and many other localities.

In laboratory studies, fusions of a Florida rock phosphate with various addition agents were made in a small furnace constructed of high temperature insulating brick and fired with natural gas. The phosphate rock and various proportions of the addition agents were thoroughly mixed, and fused in a suitable crucible in the furnace. The molten product was quenched by pouring the melt into an aqueous

cooling medium. The quenched product was dewatered, dried and analyzed.

The major emphasis in the experimental work was upon fusions using langbeinite as an addition agent since it can be obtained in commercial quantities at a low cost. Fusion of this material in various proportions with phosphate rock gave products which showed maximum P_2O_5 availability when mixtures containing at least 70 per cent langbeinite were used. The P_2O_5 availability of the products from these mixtures was 96 per cent or greater. Typical fused product from a 70 per cent langbeinite mixture contained 14.6 per cent P_2O_5, 11.4 per cent MgO, 11.6 per cent K_2O and 1.6 per cent fluorine. The P_2O_5 availability was 98 per cent, according to the procedures of the Association of Official Agricultural Chemists. The water soluble fraction, however, contained no P_2O_5. Availabilities of MgO and K_2O were at least 95 per cent, using a hot water extraction as prescribed by the A.O.A.C. The product was chalk white, soft and easily ground. Fusions of compositions below 50 per cent langbeinite could not be made successfully in the laboratory furnace because the temperatures required were above 2600° F. which was the maximum obtainable in the furnace.

Fusion of magnesium sulfate and phosphate rock gave products of complete P_2O_5 availability when mixtures containing at least 75 per cent magnesium sulfate were used.

The fusion products from mixtures of potassium sulfate and phosphate rock showed relatively low P_2O_5 availabilities, however, being only 55 per cent when 90 per cent potassium sulfate was used in the charge.

A three component study of the system $MgSO_4$-K_2SO_4-phosphate rock showed that high P_2O_5 availability was obtained when mixtures were fused whose compositions lay in an area on a triangular chart approximately bounded by the $MgSO_4$ apex and compositions containing 25-35 per cent $MgSO_4$ and various amounts of K_2SO_4.

Other addition agents were also tested, including $MnSO_4$, $MgCl_2.6H_2O$, cryolite, bauxite, potash spar, and zeolite. However, none of these could be fused successfully, because of transition to the oxide form which was infusible at temperatures obtainable in the laboratory furnace.

It was found that aqueous quenching of the molten product gave the highest P_2O_5 availabilities. When non-aqueous quenching media such as air, steam, or organic solvents were used, lower availabilities were obtained.

A pilot plant was built and successfully operated, using langbeinite and phosphate rock, at a production rate of 100 to 150 pounds of fused product per hour. A vertical gas fired shaft furnace was used with a chrome-plastic refractory hearth. No refractory corrosion was observed. There was no evidence of appreciable loss of product by volatilization.

The product was finely granulated by quenching sprays and P_2O_5 availabilities as high as 95 per cent were obtained.

A cost estimate for a proposed 100 ton per day commercial plant, located in central Iowa, indicated a production cost of $34.12 per ton of bagged product. Assuming a selling price of $38.88, based on the P_2O_5 and K_2O content only, the return on an estimated total investment of $769,000 would be approximately 5.5 per cent. Because of the magnesium content of the product and its other special properties, it is likely that a higher price could be obtained in many localities.

INTRODUCTION

During the past century the chemical fertilizer industry has grown from a small, insignificant by-product business into a large, important, and essential enterprise of national and international scope. It is now regarded as a vital industry for national health and development and represents the most important advance ever made toward providing sufficient food for the peoples of the earth (5).

By the use of fertilizers, it is now possible to bring most barren soils into high productivity, to maintain the producing capacity of fertile soils, and to raise the crop-producing powers of nearly all soils (45).

Approximately 23 elements are necessary to support plant life. The most important are nitrogen, phosphorus and potassium. These elements are called primary nutrients because they are needed in the largest amount by most plants. Sulfur, calcium, and magnesium, called secondary nutrients, are also important but are required in lesser amounts. The balance of the 23 essential elements are needed only in minute quantities and are called "trace elements". They include sodium, chlorine, silicon, iron, aluminum, manganese, copper, zinc, boron, molybdenum, carbon, cobalt, nickel, beryllium, lithium, chromium, and vanadium.

In the majority of soils phosphorus is the most deficient nutrient (33). It has been estimated that there is an annual world deficit of over three million tons of P_2O_5[1] in the soil (57). In consequence, phosphate fertilizers are being more widely applied to soils than any other type of fertilizer. At present their use is limited largely by supply rather than demand or soil requirements.

Phosphorus never occurs in nature in pure form but is found in abundance in the form of various compounds, mainly as phosphate rock. Most of the phosphorus in the rock phosphate is present as fluorapatite (29), $Ca_{10}F_2(PO_4)_6$, a compound so stable that the phosphorus is not readily available[2] as a source of plant food (55). The phosphorus in the phosphate rock can be made readily available to growing plants by destroying the fluorapatite structure and forming compounds that are soluble in the soil solutions. This may be accomplished in a number of ways:

1. Acidulation. The rock phosphate may be treated with sulfuric acid to give what is known as normal superphosphate (56, 48). This is the oldest and most widely used method of producing available P_2O_5 and the reaction is considered to be

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[1]In the fertilizer industry phosphorus is commonly expressed as the pentoxide, P_2O_5.

[2]Available phosphorus refers to its solubility in soil solutions. It is measured in the laboratory by solubility in neutral ammonium citrate or two per cent citric acid and is expressed as per cent P_2O_5.

represented by the following equation (60):

$$Ca_{10}F_2(PO_4)_6 + 6H_2SO_4 + 15H_2O = 3Ca(H_2PO_4)_2 \cdot H_2O + 6CaSO_4 \cdot 2H_2O + CaF_2.$$

A part of the CaF_2 reacts further with the acid to produce gaseous HF.

When phosphoric acid is used, the product is known as double, triple or concentrated superphosphate and the reaction is represented as (7):

$$Ca_{10}F_2(PO_4)_6 + 12H_3PO_4 + 9H_2O = 9Ca(H_2PO_4)_2 \cdot H_2O + CaF_2.$$

Nitric acid, mixed nitric and sulfuric acids, oxalic acid, and other acids may also be used to destroy the apatite structure (8, 26).

Ordinary and triple superphosphate presently account for approximately 95 per cent of all phosphatic fertilizers (57).

2. Defluorination. The phosphate rock may be defluorinated in the molten state in the presence of silica and water vapor (16). In this process the fluorine is removed from the apatite structure and not more than 10 per cent of the initial fluorine remains in the product. The reaction may be represented as:

$$Ca_{10}F_2(PO_4)_6 + xSiO_2 + H_2O = 3Ca_3(PO_4)_6 + CaO \cdot xSiO_2 + 2HF.$$

Defluorination may also be accomplished by thermal treatment of phosphate rock in the presence of silica and water vapor without fusion (30, 51, 52, 53, 65).

3. Fusion with addition agents. The phosphate rock may be fused with certain addition agents to form a glass in which the P_2O_5 is available, without substantial elimination of fluorine (28, 43, 64).

4. Production of elemental phosphorus. The phosphate rock may be heated in an electric furnace in the presence of silica and coke to get elemental phosphorus as follows (31):

$$Ca_{10}F_2(PO_4)_6 + 9SiO_2 + 15C = 3/2P_4 + CaF_2 + 9CaSiO_3 + 15CO.$$

A blast furnace may be used (15, 25) instead of an electric furnace for producing elemental phosphorus according to the above reaction but this process requires over three times as much coke, since the coke is used for thermal as well as chemical energy. In either case the elemental phosphorus is oxidized to P_2O_5 and may be absorbed in water to produce phosphoric acid or it may be reacted with rock phosphate to produce calcium metaphosphate.

$$Ca_{10}F_2(PO_4)_6 + 7P_2O_5 + H_2O = 10Ca(PO_3)_2 + 2HF.$$

The production of superphosphate by acidulation of phosphate rock with sulfuric acid is seriously limited at

present by the world sulfur shortage. With present production rates, it is estimated that the Frasch mineable sulfur will last from 11 to 25 years (61, 62). Approximately 75 per cent of the sulfur consumed in the United States is used in the manufacture of sulfuric acid, of which the fertilizer industry uses almost 45 per cent (61). With the large increase in demand for superphosphate and other phosphatic fertilizers over the past decade, there is every reason to believe that the sulfur shortage will create a desperately serious situation in the near future, unless new sources of sulfur are developed or facilities installed to produce phosphatic fertilizers without sulfuric acid. In time there will be adequate sulfur resulting from new discoveries, utilization of lower grade deposits, and recovery from by-product sources to meet the world demand (8, 63) but it is unlikely that these new sources will be brought into production at a sufficient rate to meet the requirements.

The production of triple superphosphate, made by acidulating phosphate rock with phosphoric acid, suffers from the sulfur shortage to the same extent as superphosphate if the phosphoric acid is made by the wet process, using sulfuric acid. Electric furnace acid, however, requires no sulfuric acid or sulfur and it may be used for production of triple superphosphate. The process has been well established by the Tennessee Valley Authority (7) but has not been able

to compete economically in the United States with ordinary superphosphate (8). Because of the sulfur shortage, however, this may no longer be true.

The production of fused phosphate fertilizers, either by chemical treatment with addition agents or defluorination, requires neither critical sulfuric acid nor expensive phosphoric acid. A process using magnesium silicate as an addition agent (64) has been used commercially in the United States by two plants, the Manganese Products Corporation at Seattle, Washington and the Permanente Metals Corporation near San Francisco, California. The process has also been reported in use in Japan and Formosa (9). It is adaptable, however, only to regions of low power cost and available olivine or other magnesium silicate ore. The defluorination process (27) has not been adopted commercially, in the United States, due partially to mechanical difficulties and high fuel consumption.

In the Midwest, the production of phosphatic fertilizers has been dependent on phosphate rock from Florida and sulfur from Texas and Louisiana, either as brimstone or sulfuric acid. Almost all of the production capacity in this area is as superphosphate. As a result of the critical sulfur situation, the present supply of fertilizer is impaired and any future expansion, based on sulfur uses direct or indirect, has been curtailed. Cheap electric power is generally not

available in the Midwest and consequently electric furnace phosphoric acid is not feasible in this area for triple superphosphate manufacture.

The present investigation was undertaken, therefore, to study fused phosphate fertilizer processes for possible adaptation to the Midwest. The following objectives were set forth:

1. To determine in the laboratory if langbeinite, a double sulfate of potash and magnesia, available in New Mexico, could be fused with phosphate rock to produce a product of high P_2O_5 availability.[1]

2. To determine to what extent other addition agents could be used.

3. To demonstrate the feasibility of adapting the laboratory work to a larger scale in a fuel-fired pilot plant furnace.

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[1]The term "availability" used here and throughout the thesis refers to the per cent of the total P_2O_5 which is soluble in neutral ammonium citrate or 2 per cent citric acid, as designated.

REVIEW OF THE LITERATURE

Although relatively few investigations of fusions of phosphate rock with addition agents have been reported, the work extends back at least to the beginning of the twentieth century. In 1903 Wiborgh (66) obtained a patent on a process for making fertilizer by melting acid furnace slag or Bessemer slag with phosphate rock. In the same year Wolters (68) described a process for making a product of high P_2O_5 availability by melting a mixture of natural phosphate, silicates of alkalies and silicates of alkaline earths, at a temperature above 1200° C. He found, that by fusing a mixture of the above constituents in proportions of 1.00, 0.30, and 0.60 parts respectively, the P_2O_5 content was completely soluble. Complete solubility was also obtained by fusing a mixture of phosphate rock, calcium carbonate, and silica in proportions of 1.00, 0.80, and 0.84 parts respectively but considerable volatilization of P_2O_5 occurred.

Giese and Wolters (19) in 1912 obtained a patent on the preparation of soluble phosphates by fusing rock phosphate with silicates and cooling the molten mass by a blast of air and steam. They used the proportions (a) 1.00 part rock phosphate, 0.45 part sodium bisulfate, 0.28 part limestone and 0.27 part of silica, or (b) 1.00 part rock phosphate and

0.45 part sodium calcium silicate. In 1923 Prjanischnikoff (49) made a product of high P_2O_5 availability by fusing rock phosphate with sodium carbonate in a ratio of 1.00 to 0.50. Heskett (24) in 1935 described a process in which molten phosphate rock and addition agents (silica, alumina, magnesia or alkalies) were subjected to a stream of air or steam to obtain a product of high P_2O_5 availability for fertilizer purposes.

A number of processes have been described for calcination of phosphate rock with addition agents without actually fusing the materials. In the Rhenania process (18, 42, 54) phosphate rock is calcined with an alkali, usually soda ash, and silica. A plant using this process is operating in Germany with a capacity of 100,000 tons per year (22). Raw phosphate and silica are ground together to minus 180 mesh and mixed with soda ash in a ratio of four parts of rock to one part of soda ash. About 10 per cent of water is added and the materials fed to a kiln, counter-current to combustion gases, and calcined at 1100 to 1200° C. The product is quenched with water just before it is discharged from the kiln. Plant growths have been comparable to those obtained with superphosphate and basic slag. Recently Paoloni (47) described a process in which mineral phosphates were sintered at 1200-1250° with sodium carbonate and magnesium silicate in molar proportions corresponding to P_2O_5, Na_2O, and MgO of

2:1:1 respectively. In another patent (46), he described a process for calcining Constantina phosphate with quicklime and sand in a ratio of 1.00, 0.37, and 0.30 parts respectively to obtain a product of 20 per cent P_2O_5, 90 per cent available in ammonium citrate or citric acid.

Most of these processes have the disadvantages (64) of (a) excessively large proportions of addition agents, such as calcium silicate, with high fusion costs and low P_2O_5 concentration in the products, or (b) expensive addition agents such as sodium carbonate.

About 1934 considerable interest began to be shown in the relation of fluorine content to P_2O_5 solubility. Jacob and his co-workers in the U. S. Bureau of Chemistry and Soils studied the volatilization of fluorine from phosphate rock by calcination in the presence of silica and water vapor (30, 35, 36, 51, 52, 53). Their results showed that, when thin layers of rock phosphate containing 4 to 12 per cent silica were heated in the presence of water vapor at 1400° C. for 30 minutes, 95 per cent or more of the fluorine was volatilized. Curtis (13) and Elmore (16) studied the defluorination of phosphate rock by fusion with silica and water vapor. Their studies showed that defluorination is more rapid in the molten state and that the rate of defluorination increased as the fluidity of the melt increased, increased as the water vapor content and velocity of the furnace atmosphere

increased, and decreased as the depth of molten material increased.

Defluorination by calcination is presently being used by the Coronet Phosphate Company in their plant near Plant City, Florida (37, 38, 39, 40, 65). Defluorination by fusion is being carried out in fuel-fired vertical shaft furnaces at TVA (27, 59).

Little commercial interest was shown in the fusion of phosphate rock and addition agents without substantial removal of the fluorine until the work of Walthall and Bridger in 1943 (64). They showed that the fusion of phosphate rock with magnesia and silica gave a product having a high P_2O_5 availability, yet containing approximately two-thirds of the initial fluorine. A systematic investigation of the desirable proportions of phosphate rock, magnesia, and silica (1.00, 0.24, and 0.25 respectively) showed that olivine could be used as a source of magnesia and silica. The minimum olivine-phosphate rock proportions for high availability were 0.46 to 1.00 parts respectively. Two electric furnaces were used in the course of the investigation, a Detroit rocking indirect-arc furnace and a single-electrode direct-arc furnace. The product was quenched in water. Callahan (11) described commercial facilities for fused phosphate fertilizer production, based on the findings of Walthall and Bridger, as installed by the Permanente Metals Corporation.

A cooperative research program between Manganese Products, Inc. of Seattle and the University of Washington confirmed the findings of Walthall and Bridger by additional laboratory and pilot plant work (20, 23). Results of this work indicated that:

1. A product of 95 per cent availability could be obtained by fusing phosphate rock with magnesia and silica or olivine without substantial volatilization of the fluorine.

2. The area of solubility in the MgO-SiO_2-phosphate rock system was defined by the following points, expressed as mol ratios of constituents in the products:

$\frac{MgO}{P_2O_5}$		$\frac{SiO_2}{P_2O_5}$
3.3	-	1.4
5.0	-	2.3
1.9	-	2.3
3.1	-	3.6

3. Time in the molten state had no appreciable effect on P_2O_5 availability.

4. Temperature in the range 1450°-1600° C. had no appreciable effect on P_2O_5 availability.

5. Volatilization of P_2O_5 from the melt was not evident in absence of reducing substances either at long fusion times or temperatures up to 1740° C.

6. Fluorine in excess of 0.56 mol per mol of P_2O_5 in the melt was volatilized during fusion.

7. The fused product appeared to be an amorphous glass having no crystalline structure.

8. The reversion from available to unavailable P_2O_5 took place at approximately 500° C.

9. Burned chrome, chrome cast and high alumina-zirconia were the most satisfactory refractory.

Based on these findings, the Manganese Products, Inc., Seattle, installed commercial facilities with a capacity of 50 tons of fused phosphate per day. The process and operation are described by Moulton (43).

Considerable interest in fused phosphate fertilizers has been shown recently in Japan (44, 69). Small scale studies were made using rock phosphate, serpentine and quartz in various proportions ranging from 50-60, 30-40, and 0-10 parts respectively. The mixtures were fused at 1300-1500° C. for 30-45 minutes in an electric resistance furnace and quenched in cold water, dried and ground. Best conditions were determined as molar ratios CaO/P_2O_5, MgO/P_2O_5, and SiO_2/P_2O_5 of 3.0-4.0, 2.0-3.0, and 2.0-3.0, respectively. Studies were also made using rock phosphate, serpentine and potassic liparite ($K_2O.Al_2O_3.6SiO_2$) in the ratios 50-60, 30-40, and 5-10 parts, respectively. Availabilities over 90 per cent were obtained. A ferric phosphate ore and an aluminum phosphate

ore also gave high P_2O_5 solubility when fused with serpentine or liparite in the proper molar proportions. They report, further, that the P_2O_5 solubility was not affected by ferric oxide in amounts from 2 to 5 per cent nor by fluorine as $x3(Ca, Mg)O.P_2O_5 .y(CaO.SiO_2).zCaF_2$.

Experimental work on fused phosphate in England has also been recently reported (50). Phosphate rock and serpentine were fused at 1400-1600° C. and rapidly quenched. It was found in these experiments also, that the mol ratio SiO_2/P_2O_5 should be 2.0 or greater for products of high P_2O_5 availability.

Badger and Bray in 1945 (4), studied soluble glasses as fertilizer possibilities, and suggested that, with the exception of water, organic matter and nitrogen, all of the elements required for plant growth could be incorporated into a glass. They investigated the formation of glasses, by fusion and by sintering, in the three component systems K_2O-SiO_2-phosphate rock. Their results show that rock phosphate P_2O_5 was changed to an available form by heating with potash with or without silica. The method developed consisted of low temperature sintering (800° C.). Subsequently, Cornes (12) studied the utilization of greensand as an addition agent in fusions with phosphate rock. The product contained about 12 per cent available P_2O_5 and 1.4 per cent available K_2O. Later, Schatzel (58) prepared a magnesium phosphate

fertilizer by heating by-products from the potash industry with rock phosphates at a temperature below 1000° C. The product contained 18-22 per cent P_2O_5, 12-14 per cent MgO, and 26-28 per cent CaO.

The effectiveness of magnesium silicate in forming products with high P_2O_5 availability when fused with phosphate rock led to the present study of magnesium sulfate as an addition agent. Since this compound commonly occurs in nature as langbeinite, a double sulfate of potash and magnesia, the investigation also involved the study of potassium sulfate and the combination of magnesium and potassium sulfate as found in the ore. The possibility of incorporating magnesium, potassium, and phosphorus in one fertilizer was an added objective of this study.

LABORATORY INVESTIGATION

Experimental studies were made on a small scale in the laboratory to determine the methods, compositions, and conditions necessary for the production of fused phosphatic fertilizers with high availability from phosphate rock and langbeinite, and other addition agents. For these studies a small gas-fired furnace was built and experimental fusions were made.

Materials and Procedures

Materials

The phosphate rock used in the laboratory fusions was Florida land pebble obtained from International Minerals and Chemicals Corporation, Mulberry, Florida. The rock was ground in a disc mill to the following screen analysis, determined by a 10 minute Tyler Ro-Tap separation.

Screen Mesh	Per cent of sample
+ 65	0
-65 + 100	2.6
-100 + 150	11.0
-150 + 200	24.9
-200	61.5

The major constituents of this rock were determined to be as follows:

Constituent	Per cent (dry basis)
Total P_2O_5	32.5
CaO[a]	46.9
MgO[b]	0.32
Fe_2O_3[b]	0.89
Al_2O_3[b]	0.81
CO_2[b]	2.42
F	4.40

[a]As determined by the Ames Laboratory of the Atomic Energy Commission, Ames, Iowa (reference ELC-1-244).

[b]As determined by Brunsting (10).

The langbeinite used was obtained from the Potash Division of International Minerals and Chemicals Corporation, sold under the trade name of Sul-Po-Mag. This mineral is a double sulfate of potash and magnesia ($K_2SO_4 \cdot 2MgSO_4$) mined and refined in America exclusively by International at

Carlsbad, New Mexico. It was ground in a laboratory Micro Pulverizer to the following screen analysis:

Screen Size	Per cent of sample
+ 65	10.7
-65 + 100	19.5
-100 + 150	16.1
-150 + 200	21.0
-200	32.7

The composition of pure langbeinite, commercial langbeinite (Sul-Po-Mag), and the langbeinite as received (designated as "A") is given in the following table.

Constituent	Per cent (dry basis)		
	Pure Langbeinite	Commercial Langbeinite	Langbeinite "A" as received
MgO	19.4	18.0[a]	15.7
K_2O	22.7	21.0[a]	18.4
P_2O_5	--	--	3.9

[a]IMCC specifications.

The P_2O_5 in the langbeinite as received was an impurity which was probably picked up at the supplier's packaging plant where phosphatic materials are also packaged. Subsequent shipments of langbeinite also contained P_2O_5 as an impurity. Proper account was made for this impurity in all material balances and analyses and the results verified by

using in a control fusion a mixture of reagent grade K_2SO_4 and $MgSO_4$ in the same proportions as pure langbeinite.

Analyses

The methods of analyses as set forth by the Association of Official Agricultural Chemists (2) were used for total P_2O_5, available P_2O_5, K_2O, and MgO.

When the work started, the A.O.A.C. authorized two methods for the determination of available P_2O_5 content of fertilizer. For the "Thomas" or basic slag type of phosphate, a 2 per cent citric acid solution was prescribed as a solvent, whereas a double extraction using water followed by neutral ammonium citrate solution was prescribed for other types.

Neither of these methods applied directly to fused fertilizers since they differ considerably in manufacture, structure, and composition from other phosphatic fertilizers. The fused product is similar in physical properties to a slag, therefore the 2 per cent citric acid solvent was used. MacIntire (34) proposed a modification of the A.O.A.C. procedure for fused phosphates and this method was used for the early studies.

The 2 per cent citric acid solvent has been deleted in the latest revision of A.O.A.C. Method of Analyses (3) and only the citrate solvent is authorized. Many of the early

fusions were therefore re-analyzed for available P_2O_5 using neutral ammonium citrate as solvent. Later fusions were analyzed by both methods.

Fluorine was determined by the method of Brabson, Smith and Darrow (6) using perchloric acid digestion alone. This procedure involves steam distillation, holding the perchloric acid at 135° C. for 30 minutes. Extraction was shown to be complete if a sample of 0.25 gram was used so that silica formation does not become serious.

An aliquot of the distillate was taken, neutralized and titrated with thorium nitrate solution using a sodium alizarin sulfonate indicator. The end point with this indicator is very difficult to determine. The indicator gives a neutral color at the end point which persists over quite a range and gradually changes to pink. Other indicators have been proposed (67) but all give a similarly difficult end point or require special lighting and equipment. The sodium alizarin sulfonate titration was standardized with c.p. sodium fluoride using a definite pink end point. The standardization curve is shown in Figure 1.

The end point in the lower range of fluorine contents is more readily determined than in the higher range. This gives greater accuracy in the lower ranges, below 0.2 milligram of fluorine. Since only 0.25 gram of sample is extracted, a considerable dilution is required for samples having a

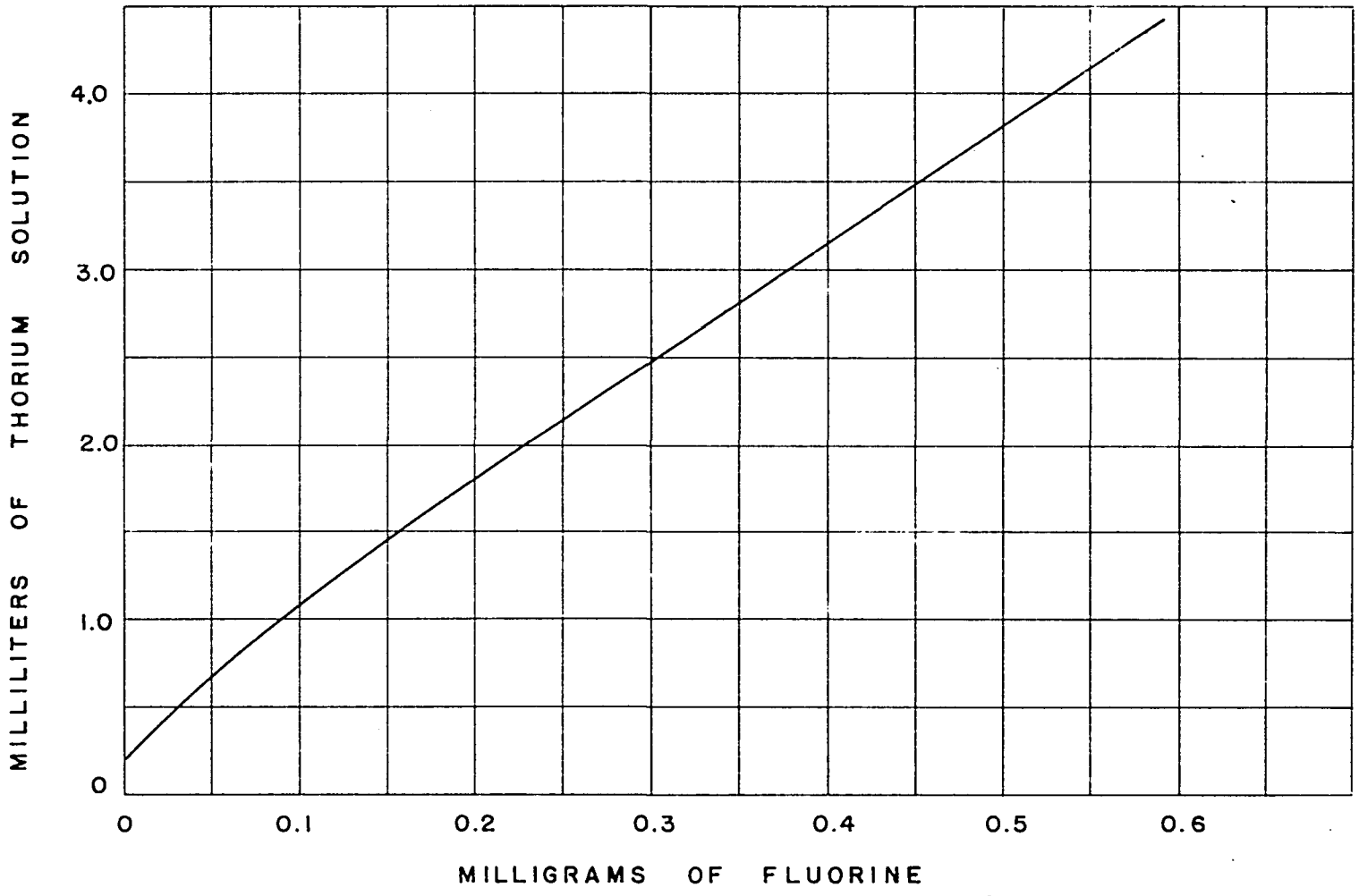


Figure 1. Standardization Curve for Fluorine Analysis.

fluorine content above 4 or 5 per cent, to get an aliquot for titration in the low range, and, consequently, the determination is more accurate for samples of low fluorine content. It is believed that fluorine contents below 2 or 3 per cent can be determined with a relative accuracy of 1 per cent.

Iron and aluminum oxide were determined according to the methods of the Association of Florida Phosphate Mining Chemists (1). Calcium oxide, magnesium oxide and carbon dioxide were made according to the A.O.A.C. Methods of Analysis (2).

Crucibles

The selection of a suitable crucible for containing the molten charge proved to be a major problem. Satisfactory crucibles had to meet the following conditions.

a. Non-reactive with the melt
b. Non-absorbent with respect to the melt
c. Resistance to thermal shock
d. Resistance to temperatures from 2000° F. to 2600° F.
e. Resistance to oxidizing atmosphere of products of combustion of gas or oil.

During the early part of the work, temperatures above

2300° F., were used and the crucible problem was acute. Various materials were tried including nickel, molybdenum and alundum. None was satisfactory. At the elevated temperatures required, the nickel crucibles either melted or disintegrated. Alundum withstood the temperature but reacted with the melt. Because of the possible reducing action of carbon graphite crucibles were not used, despite their excellence in other respects. Molybdenum crucibles pressed from thin molybdenum sheets were successfully used at temperatures of 2500° F. but they suffered severe oxidation in direct contact with the hot gases and had a life of only two or three fusions. In addition, they were expensive and not readily available.

Sample tungsten crucibles were tested and found to be superior to the molybdenum crucibles, both in life and maximum temperature. These crucibles had a life of 15 to 20 fusions and could be used at temperatures well above 2500° F. Another advantage of the tungsten crucible was its heat retention. The tungsten crucible had thick walls (1/8") for strength and upon removing the crucibles from the furnace in the process of "pouring", they retained considerable heat due to their large mass and remained a cherry red color. This heat retention kept the melt fluid and enabled better quenching. Also, with the heavy wall thickness it was found possible to clean the crucible by scraping with a spatula,

whereas the molybdenum crucible did not have sufficient wall strength to withstand scraping and had to be cleaned in weak acid.

Tungsten crucibles could not be obtained at a reasonable price, however, and it was necessary to undertake their fabrication. Tungsten powder was purchased and a steel die machined for pressing the powder into shape. The process for forming the crucibles is given in detail in Appendix A.

Zirconia crucibles have been reported satisfactory by Greaves (20) for fusing olivine and phosphate rock in atmospheres of hydrogen or nitrogen. The material was not readily available, however, and the tungsten crucibles were used for the high temperature work (above 2400° F.). Platinum crucibles were not tried since Greaves found them to be unsatisfactory.

At temperatures below 2400° F. porcelain crucibles were found to be satisfactory. Most of the langbeinite-phosphate fusions during the latter stages of the laboratory work were made in porcelain crucibles, since fusion temperatures in the critical range (60-70 per cent langbeinite) were below 2300° F. In this range the porcelain crucibles were superior to any others with regard to the criteria set forth. There was no chemical attack and the crucibles could easily be cleaned by immersing in weak acid overnight.

Laboratory furnace

For the laboratory studies, a small gas-fired refractory furnace using the principle of surface combustion[1] was constructed. Surface combustion gives an almost instantaneous reaction which releases the total chemical energy of the gaseous fuels in a small space and allows the highest reaction temperature possible.

The furnace was constructed from 12 A. P. Green No. G-32 High Temperature Insulating Brick and is shown in Figure 2. A combustion volume of 100 to 120 cubic inches was provided by forming a circular interior six inches in diameter and two brick thickness high by cutting the brick. A burner port was provided into the furnace and an opening in the top for venting the combustion gases. One of the bricks in the side of the furnace was cut so that a portion of the brick could be removed for inserting and removing the crucibles. A mirror was mounted above the furnace at a 45° angle, permitting visual inspection of the crucible contents at all times through the opening in the top of the furnace. An ordinary glass blowing gas-air laboratory burner was used. Temperatures were measured by a platinum-platinum 10 per cent

[1]The name Surface Combustion originated in England and was applied to the catalytic action of certain metals and incandescent refractory surfaces upon the combustion of gas and air mixtures.

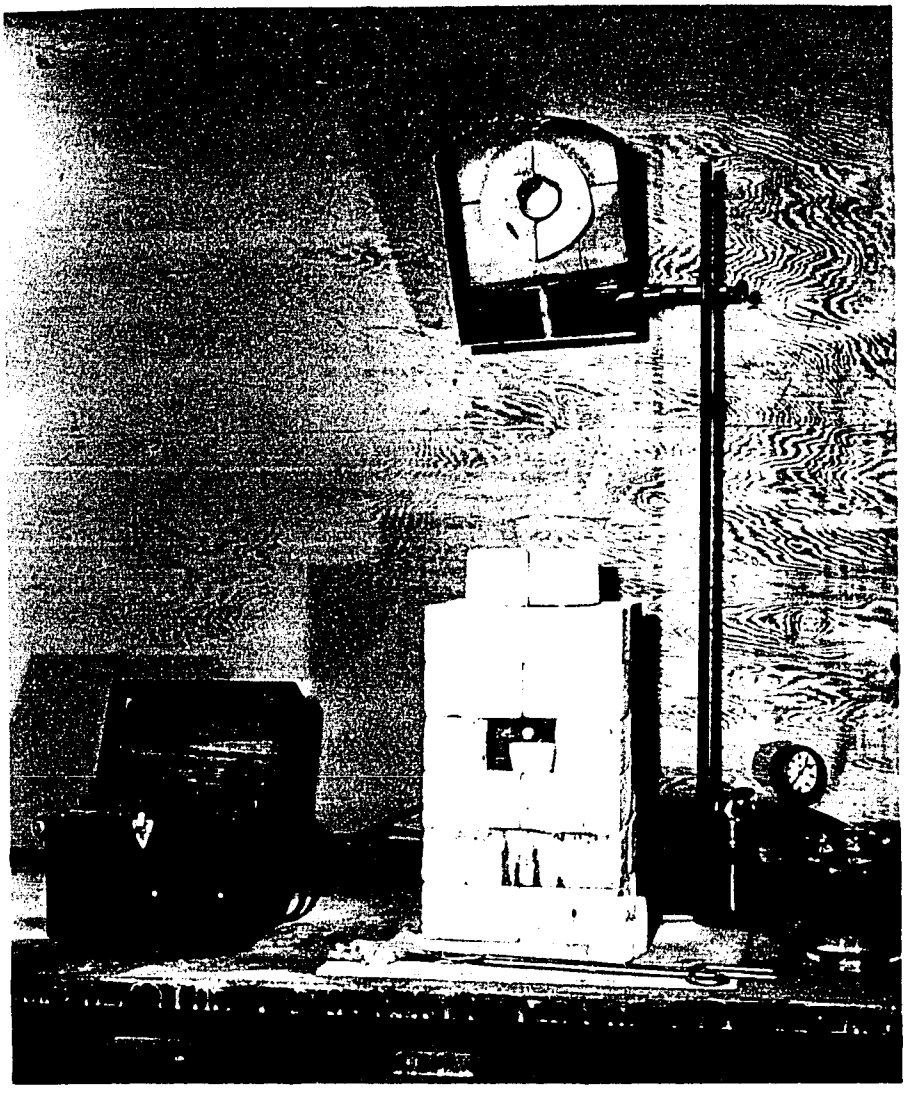


Figure 2. Laboratory Fusion Furnace

rhodium thermocouple in a sillmanite tube mounted above the crucibles and connected to a Leeds and Northrup Model 8657-C portable potentiometer as shown in the photograph. Temperatures of 2600° F. could be reached in a period of 15-30 minutes without preheating the air. Temperatures above 3000° F. could be obtained by bleeding pure oxygen into the air line.

Fusion procedure

Phosphate rock was mixed with various proportions of addition agents (langbeinite, $MgSO_4$, K_2SO_4, etc.) in either 10 or 20 gram charges. To insure uniformity, the materials were weighed into glass stoppered weighing bottles and mixed by rolling the bottles on a table or other flat surface. Very thorough mixing was obtained with no loss of material. The mixed charge was transferred to a crucible or boat which was inserted into the furnace for melting.

By means of the mirror mounted above the furnace visual inspection of the crucible charge could be made at all times and the progress of fusion noted. Temperature and appearance of the charge, or melt, were recorded as a function of time.

During the process of fusion, melting first took place near the walls of the crucible, as could be seen in the mirror, and then proceeded toward the center of the mass. Bubbles appeared throughout the charge as it melted. When

the bubbles stopped appearing the charge was considered to be initially fused. It was left in the furnace from two to five minutes longer to insure complete fusion and was subsequently removed by a pair of tongs and quenched by pouring into a cooling medium, either air, steam, water or other liquid. Water quenching was found to be superior for these studies and was used for most of the experimental fusions.

The quenched product was filtered, dried, and analyzed according to the analytical methods previously described.

Experimental Results

The experimental fusions were primarily concerned with mixtures of phosphate rock and (a) langbeinite, (b) pure K_2SO_4 and $MgSO_4$ in varying proportions, or (c) other addition agents. The major emphasis was upon the fusions with langbeinite because of its availability in commercial quantities at a low cost. Fusions of the pure components were made to extend the limits of solubility to compositions not afforded with langbeinite. Other addition agents were also used to test various possibilities.

Fusion studies with phosphate rock and langbeinite

Melting points. Melting points of the langbeinite and mixtures of langbeinite and phosphate rock were needed to

establish optimum operating conditions and to prescribe materials of construction.

The common methods for determining the melting points of a mixture of powdered materials are (a) the drip point method, and (b) the time-temperature cooling curve method. In the first method, the mixture of materials is pelletized, drilled for a thermocouple and the melting point observed as the temperatures at which the pellet melts and drips from the end of the thermocouple. In the second method, a thermocouple is inserted in a mixture of the materials or in the pure material and the time-temperature relationship developed as the material passes from the solid state to the liquid state. The latter method was used in the present work.

A small furnace for determining melting points was constructed similar to the one shown in Figure 2. A crucible containing 100 grams of the sample was suspended in the furnace so that it would be heated uniformly from the sides and bottom. A chromel-alumel thermocouple was inserted into the sample and the leads brought out through a brick at the top, thus limiting the heat flow into the sample through the leads. A Fisher and Porter laboratory Flowrator was installed on the air and gas inlets to the burner for controlling the heating rate. Very accurate furnace control was obtained in this manner and the melting point curves of Figures 3 through 10 were determined. Figure 3 showing the

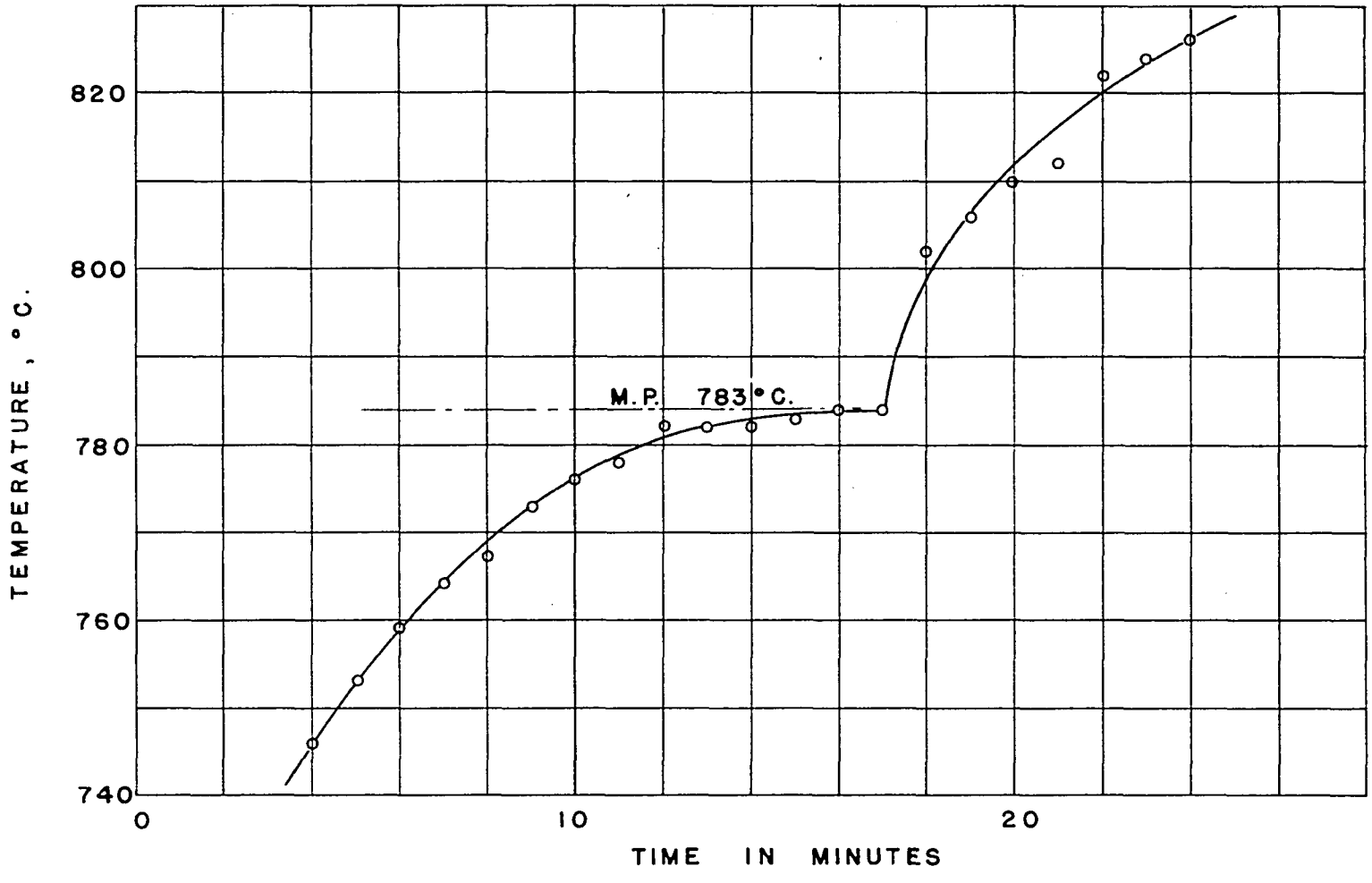


Figure 3. Melting Point Curve of Potassium Chloride

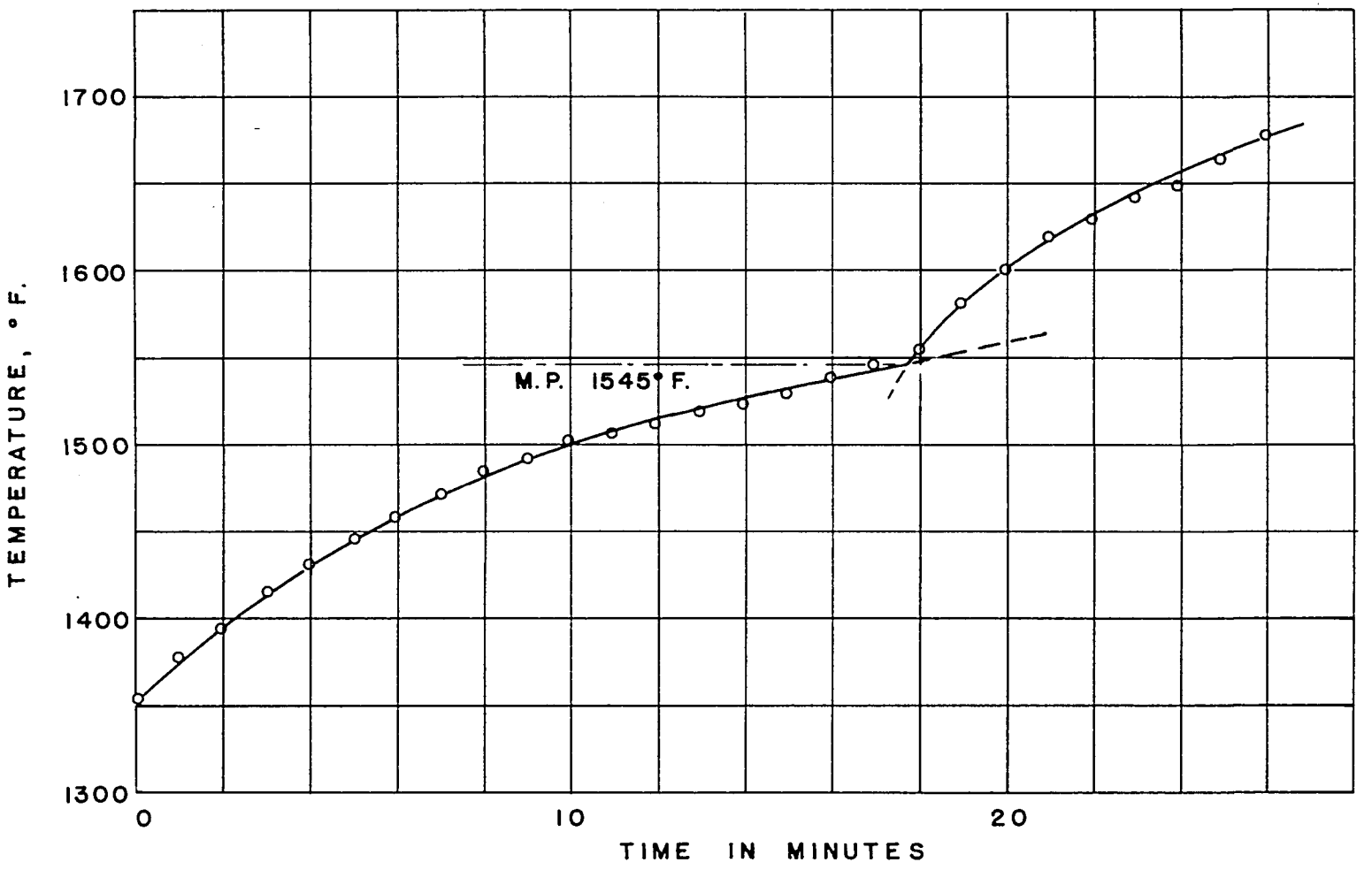


Figure 4. Melting Point Curve of Langbeinite "A"

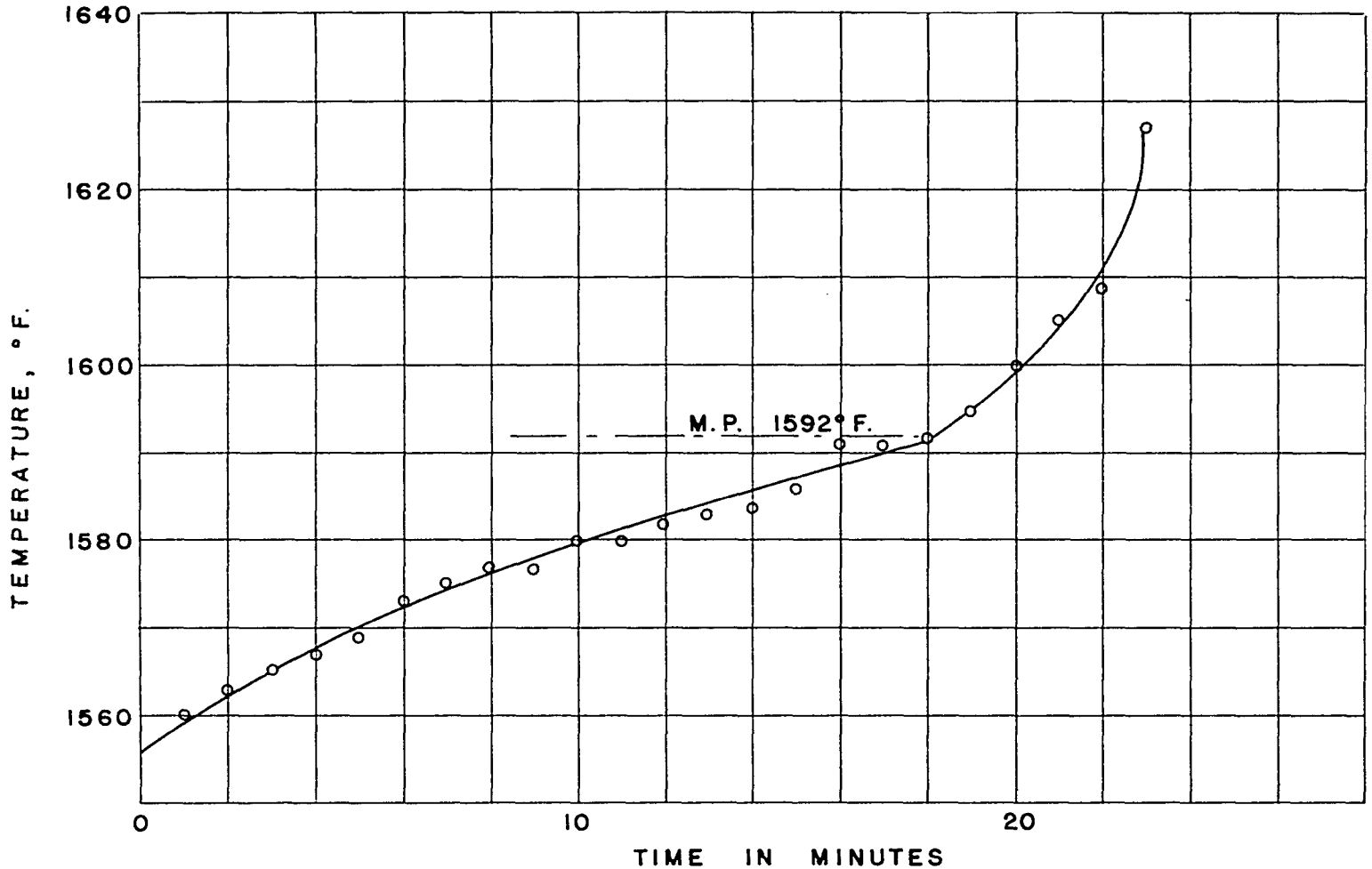


Figure 5. Melting Point Curve of a Mixture Containing 90 Per Cent Langbeinite "A" and 10 Per Cent Phosphate Rock

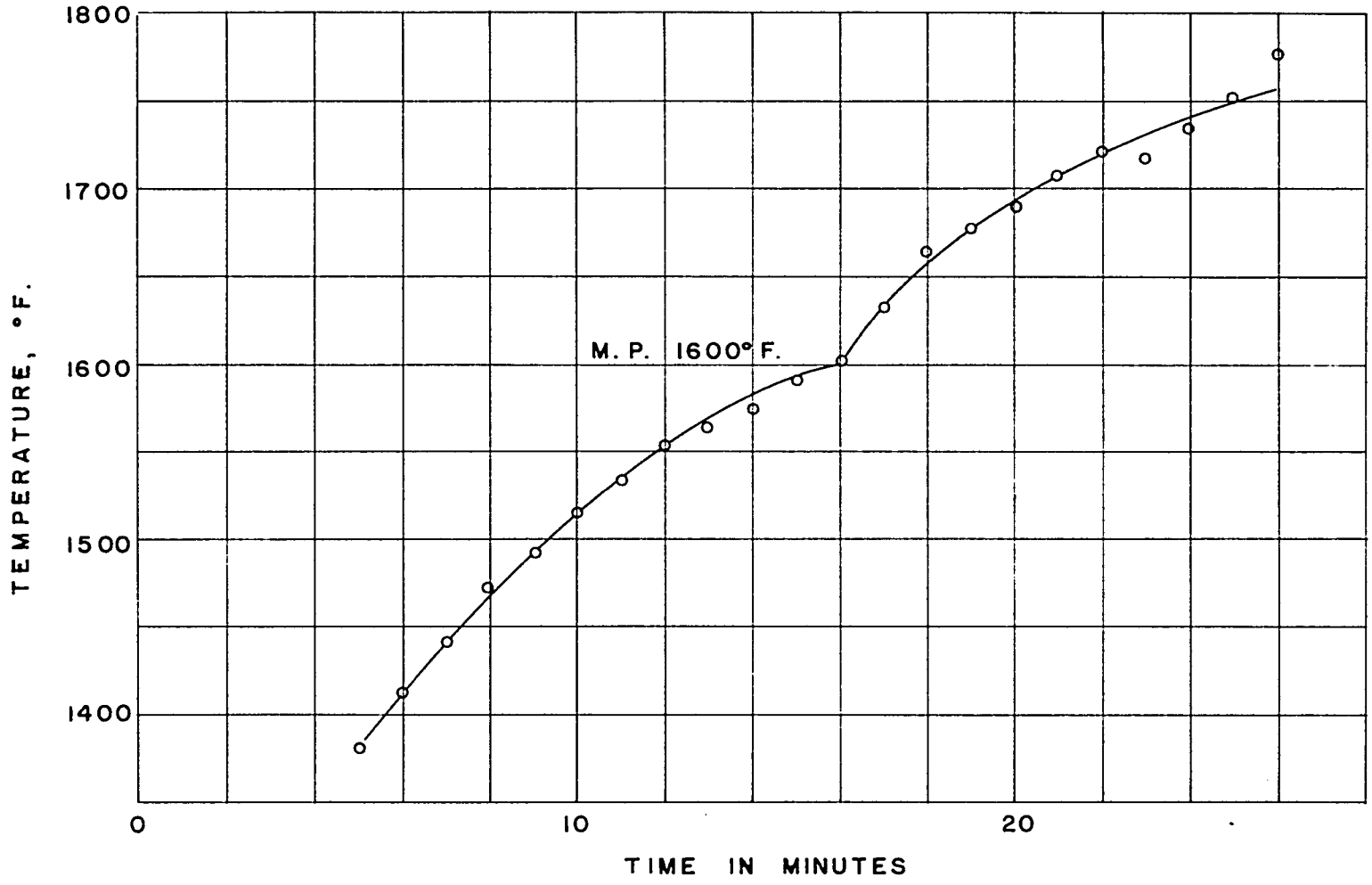


Figure 6. Melting Point Curve of a Mixture Containing 80 Per Cent Langbeinite "A" and 20 Per Cent Phosphate Rock

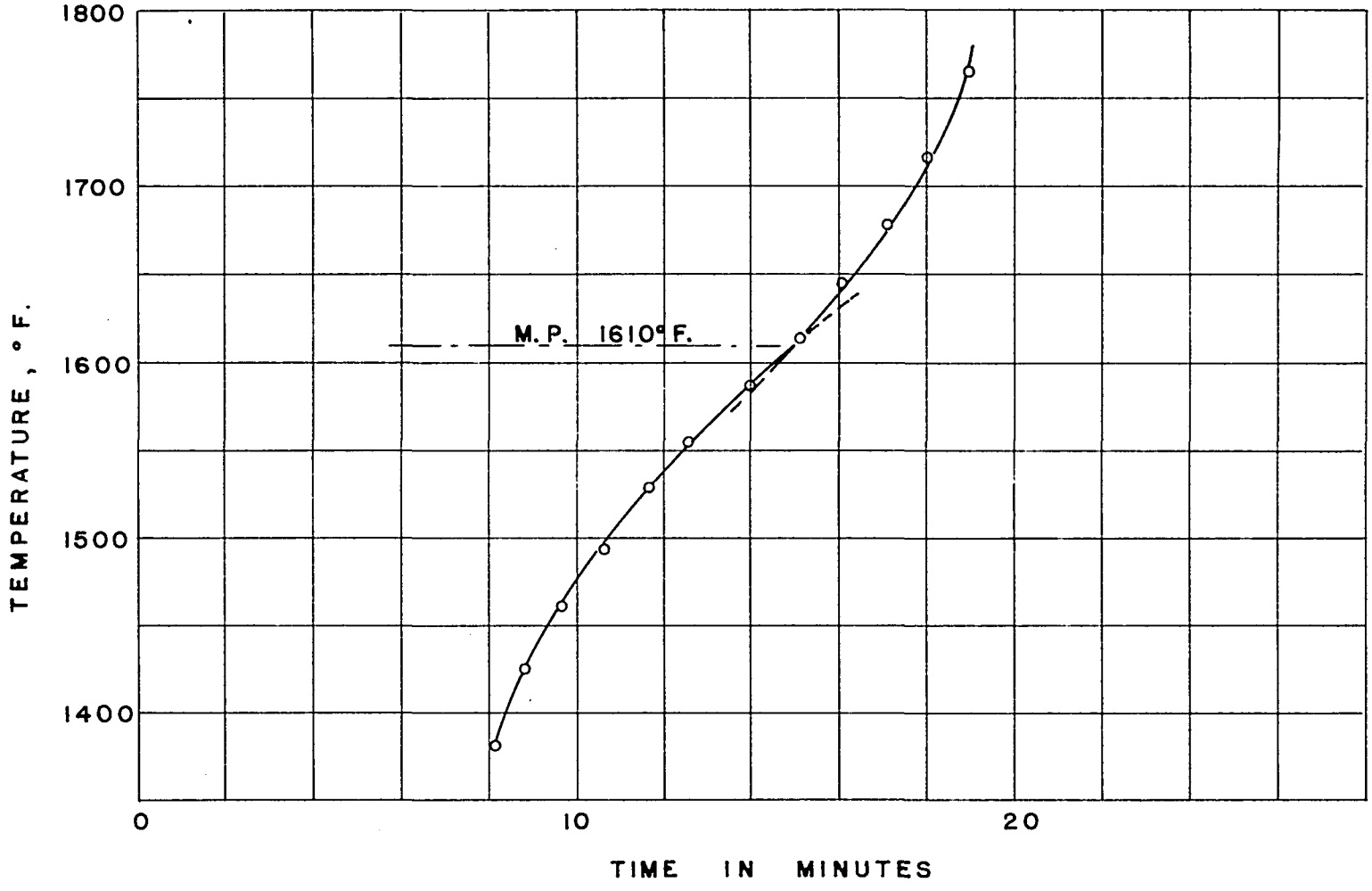


Figure 7. Melting Point Curve of a Mixture Containing 70 Per Cent Langbeinite "A" and 30 Per Cent Phosphate Rock

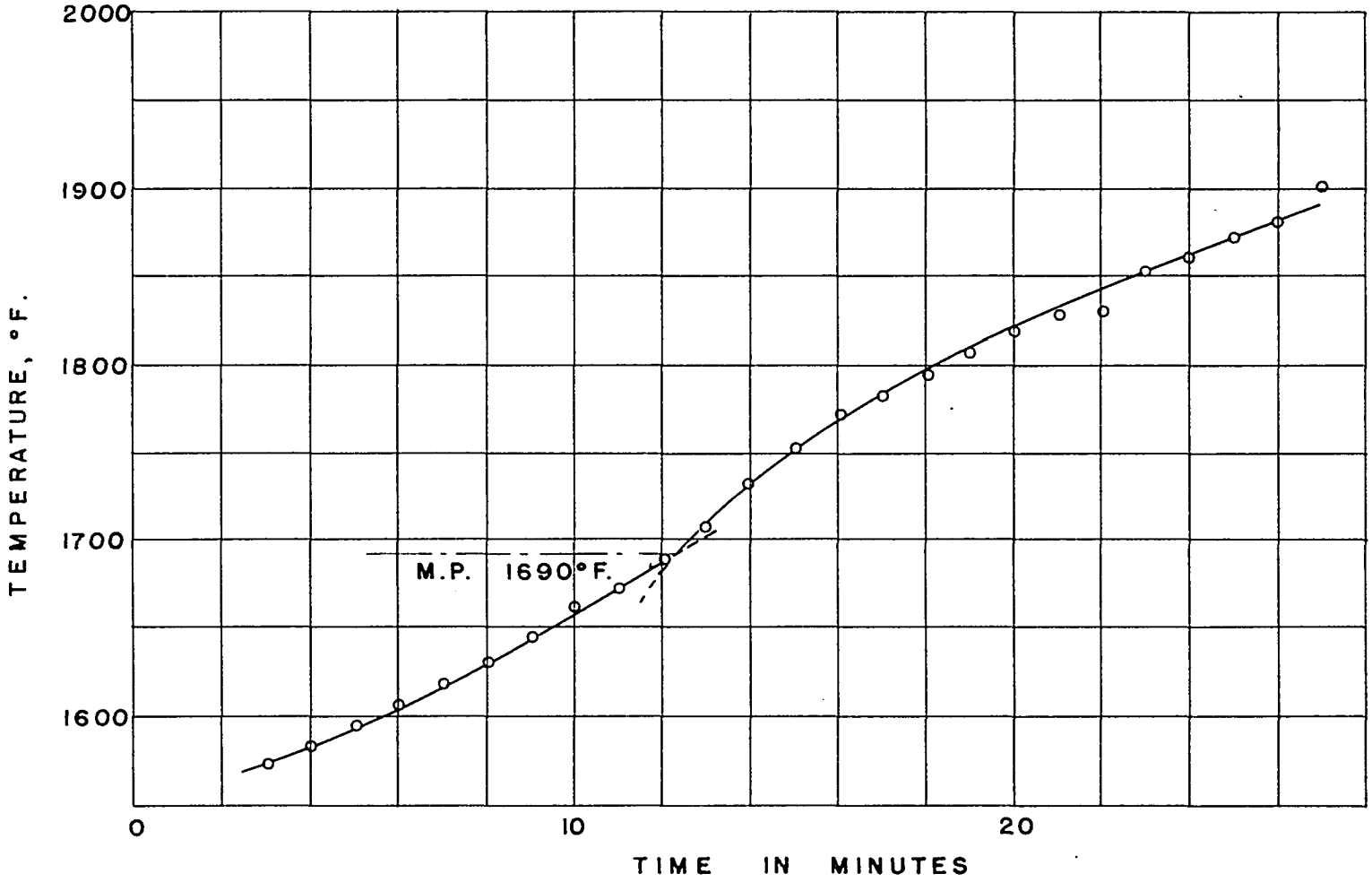


Figure 8. Melting Point Curve of a Mixture Containing 60 Per Cent Langbeinite "A" and 40 Per Cent Phosphate Rock.

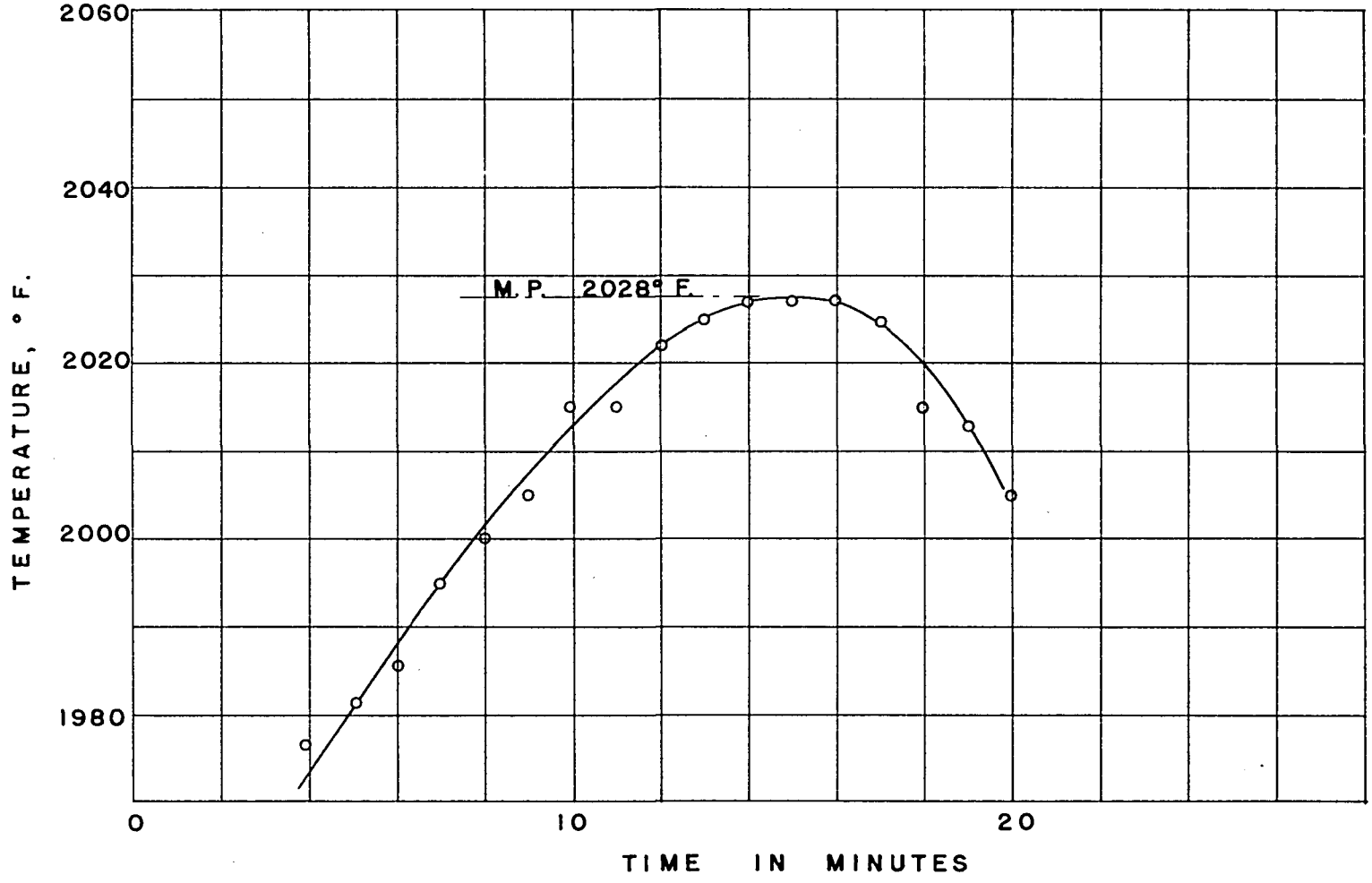


Figure 9. Melting Point Curve of a Mixture Containing 40 Per Cent Langbeinite "A" and 60 Per Cent Phosphate Rock

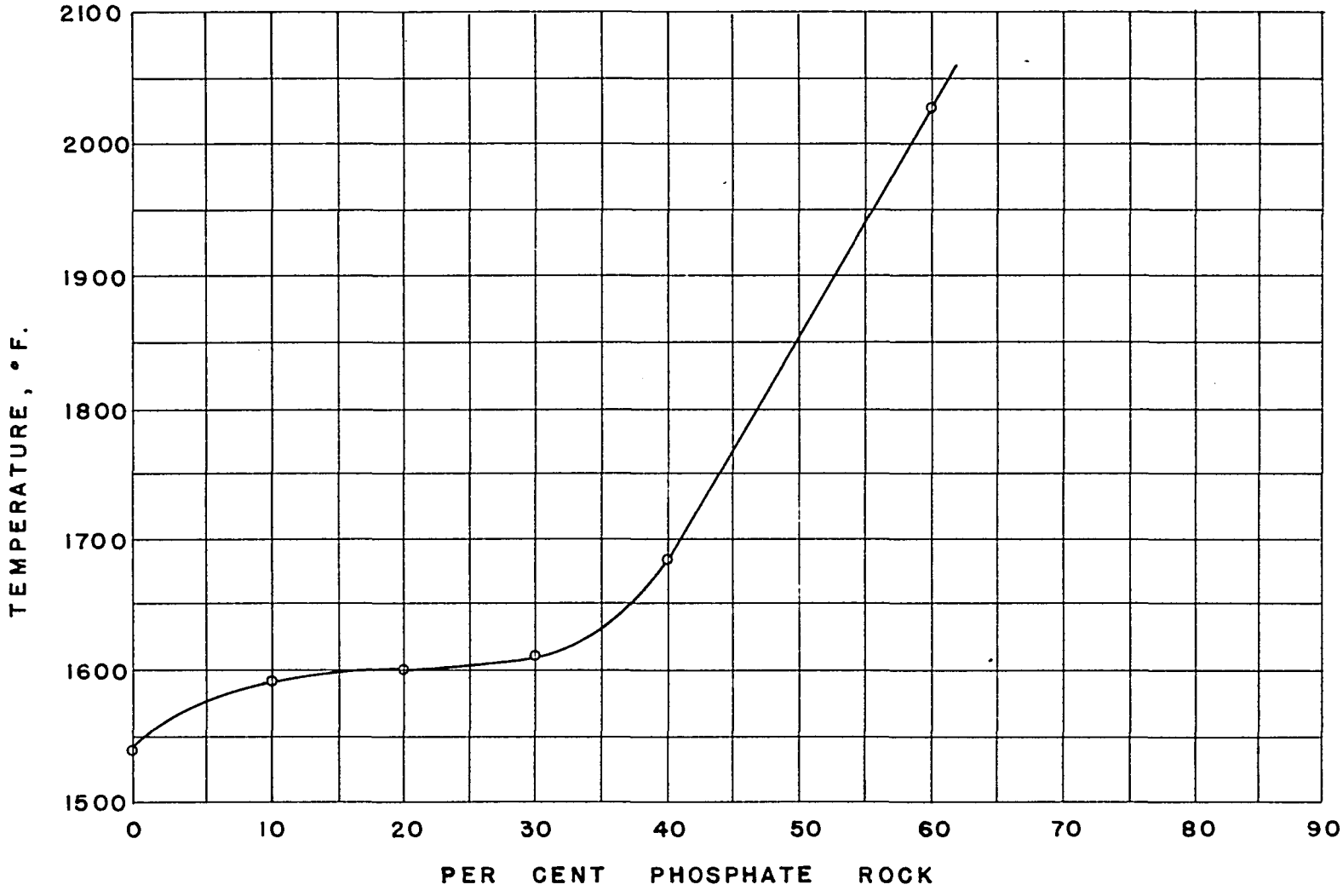


Figure 10. Variation of Melting Points of Langbeinite-Phosphate Rock Mixtures with Composition

melting points of pure KCl was made as a control. The experimental value of 783° C. agrees very closely with the reported (32) value of 790° C.

The melting point curve of langbeinite "A" is shown in Figure 4. The actual melting point apparently took place over five to 10 minutes without any plateau in the time-temperature curve. Day and Allen (14) experienced this same type of behavior with various feldspars and defined the melting point as that point where the rise in temperature is the slowest, i.e., the inflection point in the curve. Using this definition, the melting point of langbeinite "A" may be stated as 1545° F. This value does not compare to the literature value of 1706° F. for pure langbeinite (41) and shows the effect of impurities, as previously noted.

Figures 5 through 9 show the melting points, defined as the inflection point in the time-temperature curve, for various compositions of the langbeinite and phosphate rock.

Figure 10 is a plot of the melting points of the various mixtures against composition. It shows a definite increase in melting point with mixtures containing less than 70 per cent langbeinite. As will be pointed out later, mixtures containing less than 70 per cent langbeinite did not give maximum P_2O_5 availability when fused. The bubbling during fusion at the 70 per cent composition was considerably more violent than at other compositions.

Fusions of phosphate rock and langbeinite "A". In the early studies of langbeinite and phosphate rock fusions, mixtures containing from 20 to 80 per cent langbeinite "A" were tried. Compositions containing less than 50 per cent langbeinite "A" were very difficult to fuse in the gas furnace due to the high temperatures required (above 2500° F.). At these high temperatures, crucible materials became a limiting factor and the work in this range was abandoned.

In view of physical limitations in regard to fusions in the lower range of langbeinite compositions, calculations were made of the mol ratios of MgO and K_2O to P_2O_5 for langbeinite "A"-phosphate rock mixtures. The ratios are shown in Table 1.

Walthall and Bridger (64) showed that a minimum of 0.46 parts of olivine per part of phosphate rock was necessary to obtain high P_2O_5 availability in the fused product. This is equivalent to MgO/P_2O_5 and SiO_2/P_2O_5 ratios of approximately 2.2. The work of Greaves (20) substantiated this.

In the langbeinite-phosphate rock mixtures the SiO_2/P_2O_5 ratio is constant for all compositions, being that of the phosphate rock itself. The MgO/P_2O_5 ratio, however, is greater than 2.0 only for mixtures containing more than 60 per cent langbeinite.

As previously shown, melting temperatures of the langbeinite-phosphate rock mixtures were reasonably low at high

Table 1. Calculated Molar Ratios of MgO and K_2O to P_2O_5 for Various Phosphate Rock-Langbeinite "A" Mixtures

Basis, 100 grams of the mixture

% Langbeinite "A"	% Phosphate Rock	P_2O_5		MgO		K_2O		MgO / P_2O_5	K_2O / P_2O_5
		gms.	mols	gm.	mols	gm.	mols		
0	100	32.5	.229	0	0	0	0	0	0
10	90	29.6	.209	1.6	.040	1.9	.020	.191	.096
20	80	26.8	.189	3.2	.079	3.7	.039	.418	.206
30	70	23.9	.168	4.7	.117	5.6	.060	.696	.357
40	60	21.1	.149	6.3	.156	7.5	.080	1.049	.537
50	50	18.3	.129	7.9	.196	9.3	.099	1.52	.768
60	40	15.3	.108	9.4	.233	11.2	.119	2.16	1.10
70	30	12.4	.087	11.0	.273	13.1	.139	3.14	1.60
80	20	9.6	.068	12.6	.313	15.0	.159	4.61	2.34
90	10	6.8	.048	14.1	.350	16.8	.178	7.30	3.71
100	0	3.9	.028	15.7	.390	18.4	.195	13.9	6.97

langbeinite compositions and with composition of langbeinite above 50 per cent, porcelain crucibles could be used.

Two series of fusionswere subsequently made with compositions ranging from 50 per cent to 90 per cent langbeinite. Good melts were obtained which could be readily poured. A stream of air, directed into a metal crucible set in water, was used to quench the melts as they were poured into the crucible. The results of these fusions are given in Table 2. None of the fusions, however, could be considered important as a fertilizer composition because of the low P_2O_5 availability and it was decided to try quenching in water.

Two identical samples were prepared, containing 70 per cent langbeinite, and both were fused using identical procedures and conditions. One sample was quenched in a stream of air, the other was quenched in water. Analysis showed the following:

Fusion	Langbeinite (%)	Quench	% P_2O_5 Total	% P_2O_5 Available	P_2O_5 Availability (% of Total)
47-1	70	Air	13.1	10.4	79
47-2	70	Water	14.1	14.1	100

These fusions showed that water quenching was necessary to give high P_2O_5 availability in the product. The air quenched sample was 79 per cent available, while the water quenched sample was 100 per cent available with respect to

Table 2. Composition of Products from Fusions of Phosphate Rock with Langbeinite "A" Quenched in Air

Fusion	Per Cent Langbeinite "A"	Temp. (° F.)	Product Composition Per Cent P_2O_5		Availability (% of Total)
			Total	Available	
11	20	2400	29.7	10.8	36
12	40	--	26.8	9.9	37
13	50	--	17.8	9.5	53
14	60	2200	14.8	9.1	62
26	60	2100	15.6	8.0	52
36	60	2020	15.8	7.3	47
27	70	1900	12.0	7.9	65
37	70	2160	12.6	9.4	75
15	80	2200	9.2	6.7	73
28	80	1900	9.3	7.5	81
38	80	2050	9.6	8.2	86
29	90	1900	6.7	5.9	88
39	90	2100	7.0	6.3	90

P_2O_5.

To demonstrate this effect, a series of fusions was made with initial compositions ranging from 50 to 90 per cent langbeinite and quenched in distilled water. The product was filtered immediately, dried in a constant temperature oven and analyzed for total and available P_2O_5 according to A.O.A.C. methods. The results are given in Table 3.

Table 3. Compositions of Products From Fusions of Phosphate Rock with Langbeinite "A" Quenched in Water

Fusion	Langbeinite "A" (%)	Temp. (°F.)	Product Composition Per Cent P_2O_5		Availability (% of Total)
			Total	Available	
65-1	50	2125	19.7	8.4	43
65-2	50	2125	19.7	8.8	45
66-1	60	2030	16.8	10.0	60
66-2	60	2030	16.8	11.0	65
860	60	2165	16.6	12.7	77
862	62	2175	16.0	12.9	81
864	64	2130	15.0	12.2	82
866	66	2080	14.5	13.3	91
47-2	70	2025	14.1	14.1	100
57	70	--	12.4	11.9	96
67-1	70	1965	14.0	13.5	96
67-2	70	1965	13.9	14.1	100
68-1	80	2040	11.6	11.2	97
68-2	80	2040	11.2	12.1	100
58	80	--	10.4	10.7	100
59	90	--	12.0	11.7	98
69	90	1995	8.6	8.2	96

Figure 11, plotted from the data of Table 3, shows that maximum availability occurred at a minimum composition of 70 per cent langbeinite "A". At the composition the P_2O_5

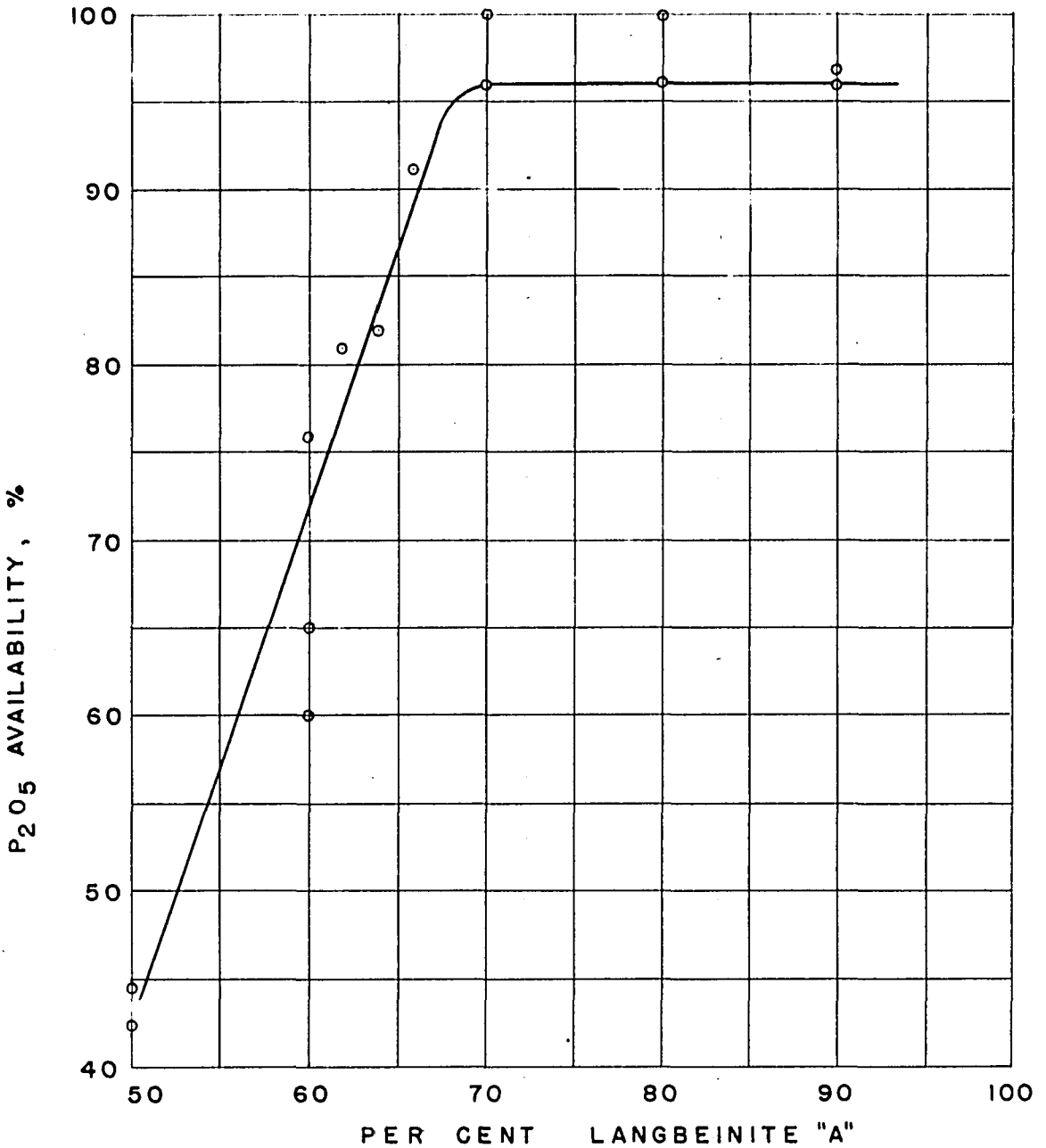


Figure 11. Effect of Composition on P_2O_5 Availability of Langbeinite "A"-Phosphate Rock Fused Products

availability was at least 96 per cent. Compositions containing more than 70 per cent langbeinite "A" gave fusion products with availabilities of 96 to 100 per cent.

Product compositions from typical fusions of a charge containing 70 per cent langbeinite "A" are given in Table 4 together with the solubilities of the major constituents and the mol ratios of MgO and K_2O to P_2O_5. The mol ratios of MgO and K_2O to P_2O_5 in the charge were 3.14 and 1.60 respectively (Table 1). These ratios were lower in the product as shown in Table 4, being 2.63 and 1.11 for fusion 1370. This reflects a loss, either in the quench water or by volatilization.

To determine the extent of losses by volatilization and solution in the quenching water material balances were computed for P_2O_5, MgO and K_2O for fusions 1370 and 1470, and are presented in Table 5. The figures represent average values for the fusions and show very little loss by volatilization or dust loss.

The loss of MgO and K_2O in the quench water was appreciable, however, being 5.4 and 17.4 per cent respectively. This was expected to a certain extent since the langbeinite itself is soluble in water and the MgO and K_2O in the product were above 95 per cent soluble in hot water according to the A.O.A.C. procedures. Solution in the quench water could be

Table 4. Composition of Products From Fusions of Phosphate Rock with Langbeinite "A"

Fusions of 70% Langbeinite "A" and 30% Phosphate Rock Quenched in Water

Fusion	Product Composition (%)				MgO	K_2O	Solubility (% of Total)		
	P_2O_5	MgO	K_2O	F	P_2O_5	P_2O_5	P_2O_5[a]	MgO[b]	K_2O[b]
1370	15.7	11.8	11.6	1.6	2.63	1.11	98.0	97.5	94.0
1470	15.6	11.9	11.5	1.6	2.68	1.11	97.0	100.0	95.0
1070	14.5	—	—	—	—	—	98.0	—	—
1170	14.6	11.4	11.4	—	2.47	1.17	99.6	99.0	92.0

[a]Solubility determined by 2% citric acid

[b]Solubility determined by hot water (A.O.A.C. par. 2.41a)

Table 5. Material Balances of Typical Fusions of Phosphate Rock and Langbeinite "A"

	Average values from fusions 1370 and 1470[a] (All figures in grams)		
	P_2O_5	MgO	K_2O
In			
Phosphate Rock	1.95	0.02	0.00
Langbeinite "A"	.70	2.21	2.58
Total	2.65	2.23	2.58
Out			
Product	2.61	2.11	2.02
Quench water	.00	.12	.45
Loss	.04	.00	.11
Total	2.65	2.23	2.58
% Loss	1.5	0.0	4.3

[a]Charge composition of 70 per cent langbeinite "A" and 30 per cent phosphate rock. Total weight of 20 grams.

minimized by reusing the quench or saturating it initially with langbeinite.

Table 5 indicated that the P_2O_5 in the product was not water soluble since none appeared in the quench water. To verify this analysis was made of the product for water soluble fraction according to the accepted A.O.A.C. procedures. The water soluble P_2O_5 was negligible.

Fusion studies with phosphate rock and other addition agents

To show the effect of potassium and magnesium sulfate separately, two series of fusions were made using

(1) phosphate rock and $MgSO_4$ and (2) phosphate rock and K_2SO_4. The molten products were quenched in water. Results of these fusions are given in Tables 6 and 7 and have been plotted in Figures 12 and 13.

The availability curve of $MgSO_4$ and phosphate rock, Figure 12, shows complete P_2O_5 solubility in the product when mixtures containing 75 per cent or more $MgSO_4$ were fused. The $MgSO_4$ melts were very fluid and easily poured from the crucible. In all cases, the temperature of the melt was below 2400° F.

The K_2SO_4 phosphate rock fusions, Figure 13, show rather poor availabilities, although very fluid melts were obtained.

Other addition agents were also tried in an attempt to determine what isomorphous substitution in the apatite structure would give a product of high availability of P_2O_5. On the hypothesis that the magnesium ion influences the structure so that high availability obtains, it was felt that the same result might be obtained with other ions having the same coordination number, that is, form the same crystal lattice. From a consideration of the radius ratio, Mg, Al, Fe, Mn, all have the same coordination number and it was decided to try addition agents containing these ions.

Cryolite ($3NaF.AlF_3$) was used in a series of fusions as a source of Al ion with the following results.

Table 6. Analyses of Products of Fusions of Phosphate Rock and Magnesium Sulfate ($MgSO_4$) Quenched in Water

Fusion	$MgSO_4$ (%)	Temperature	Product Composition (%)		Availability (% of Total)
			Total P_2O_5	Available P_2O_5	
Y-460	60	2135	14.2	11.7	82
Y-465	65	2130	11.9	9.3	78
Y-670	70	2185	10.7	9.4	87
Y-370	70	2245	10.8	9.4	87
Y-475	75	2080	8.5	7.7	97
Y-375	75	2225	12.2	12.4	100
Y-480	80	2110	6.3	6.1	97
Y-280	80	2100	7.5	7.2	96
Y-485	85	--	6.3	6.2	99
Y-490	90	2110	3.4	3.4	100
Y-495	95	--	2.4	2.4	100

% Cryolite	Temperature	% Availability
50	--	22.2
60	1775° F.	27.4
70	1780	40.1
75	1780	41.5
85	1775	56.3
90	1650	81.2

Table 7. Composition of Products from Fusions of Phosphate Rock with Potassium Sulfate (K_2SO_4) Quenched in Water

Fusion	K_2SO_4 (%)	Product Composition (%)		Availability (% of Total)
		Total P_2O_5	Available P_2O_5	
K26	60	12.9	3.4	26
K27	70	12.5	4.0	32
K28	80	10.7	4.6	43
K29	90	8.8	4.8	55

The melts were easily obtained but some difficulty was experienced during quenching. Twenty gram samples were used for the fusions and the melt was quenched in two liters of distilled water. On three occasions when the melt was poured into the water an explosion took place. These explosions were forceful enough to shatter a glass beaker and spray water over an area approximately 10 feet in diameter. As a check, two 10 gram samples containing 65 per cent cryolite

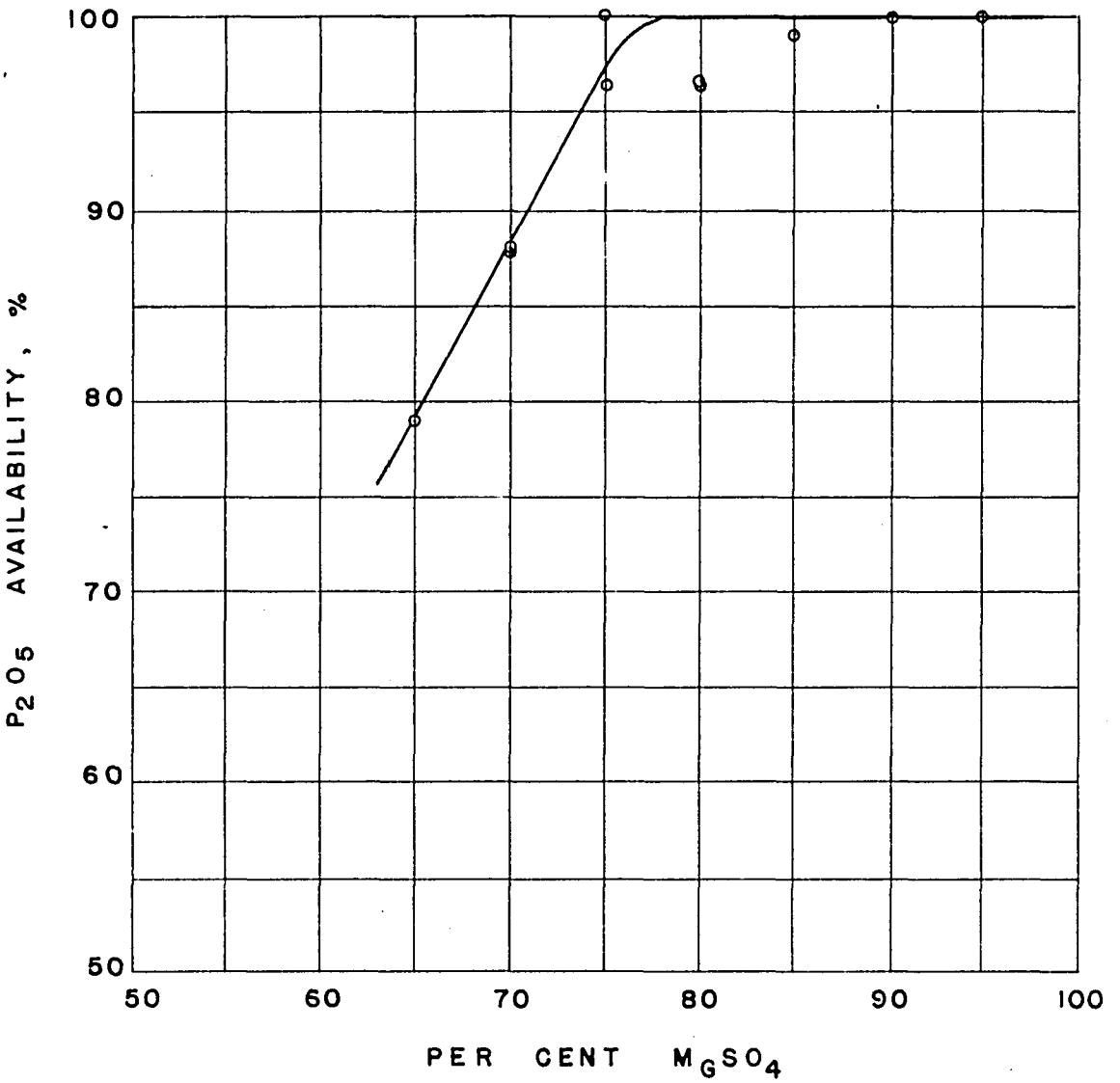


Figure 12. Effect of Composition on P_2O_5 Availability of $MgSO_4$-Phosphate Rock Fused Products

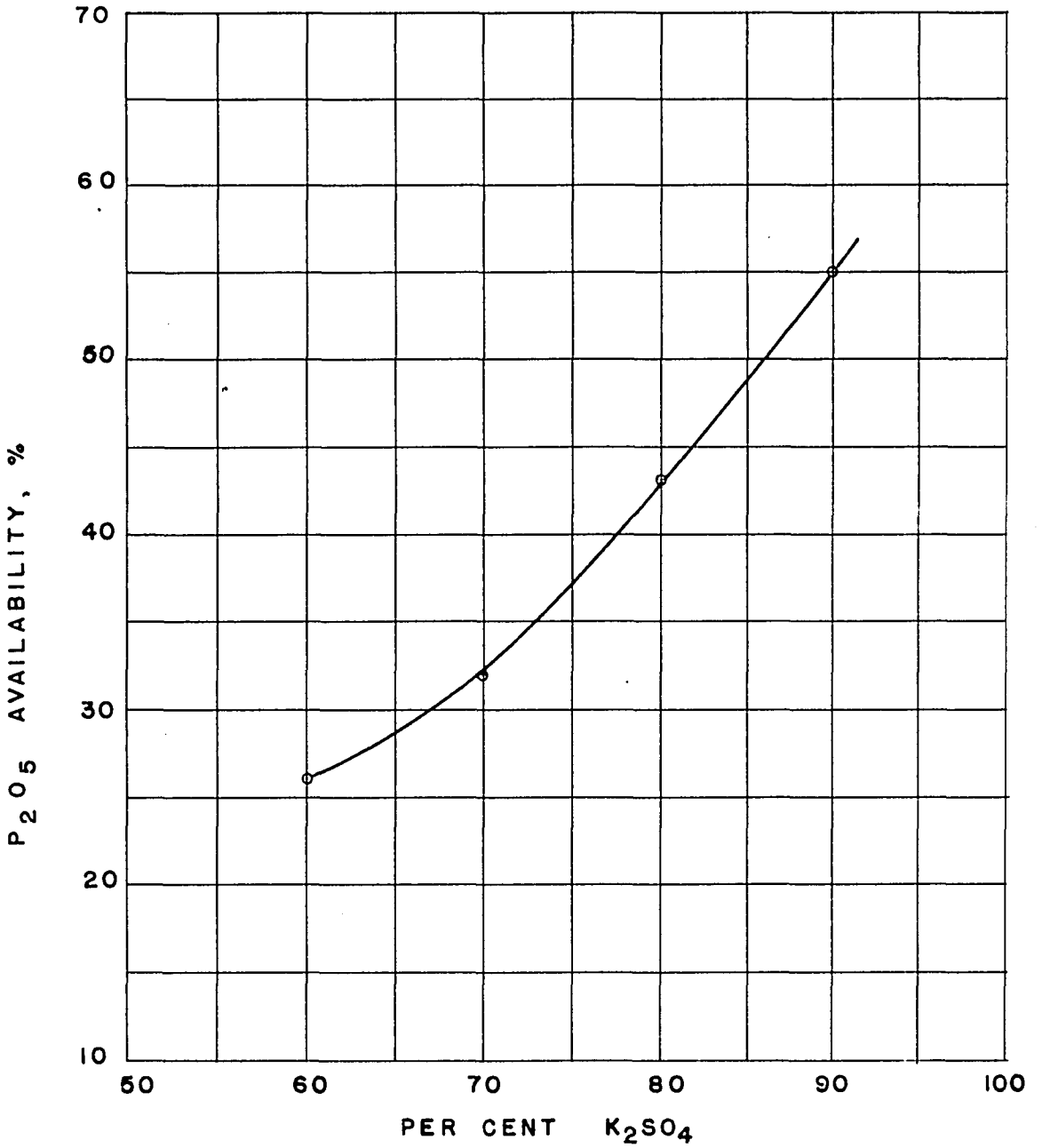


Figure 13. Effect of Composition on P_2O_5 Availability of K_2SO_4-Phosphate Rock Fused Products

were fused and quenched in water. One exploded, the other did not. The cause of the explosions is not known.

Attempted fusions with $MnSO_4$ met with failure due to transition to the oxide form which was infusible with temperatures obtainable in the gas-fired furnace. Likewise bauxite, potash spar, and zeolite could not be fused at the temperatures obtainable although various proportions of each were tried with phosphate rock.

Magnesium chloride was tried as an addition agent in an attempt to exclude the effect of the sulfate ion present in the langbeinite and K_2SO_4 fusions. The only form of $MgCl_2$ available was the hexahydrate $MgCl_2.6H_2O$. It was hoped that this material could be used directly in the fusions. However, it proved impossible to obtain fusions with the hydrate due to its change to the oxide form. As is well known, four of the waters of crystallization can be removed easily but the other two must be removed under an atmosphere of HCl. Thus it is probable that an HCl atmosphere would be necessary to obtain $MgCl_2$ fusions.

Fusion studies with the three component systems K_2SO_4-$MgSO_4$-phosphate rock

Fusion studies were made using phosphate rock and varying proportions of K_2SO_4 and $MgSO_4$ to determine the region of

maximum availability with respect to P_2O_5. Sixteen compositions, covering the range of critical solubilities, were chosen as shown on the triangular diagram, Figure 14. Each composition was expressible as a mixture of a base composition of K_2SO_4 and $MgSO_4$ with varying proportions of rock, shown by the tie lines from the phosphate rock apex to the K_2SO_4-$MgSO_4$ base at compositions 1, 2, 3, and 4. Base composition 3 (58 per cent $MgSO_4$) is equivalent to the composition of pure langbeinite.

Each of the 16 compositions was made up separately in 20 gram mixtures from the correct proportions of the three components rather than from a prepared base composition and varying proportions of rock. All samples were fused under as nearly identical conditions as possible and quenched immediately in distilled water. The quenched product was filtered, dried, and analyzed for available and total P_2O_5. Available P_2O_5 was determined by 2 per cent citric acid solubility and also by neutral ammonium citrate solubility as described previously. Duplicate fusions were made at each composition. The results are shown in Table 8. The availabilities have also been shown on Figure 14 at each composition as well as the availabilities for the two component systems, phosphate rock-$MgSO_4$ and phosphate rock-K_2SO_4 from Tables 6 and 7.

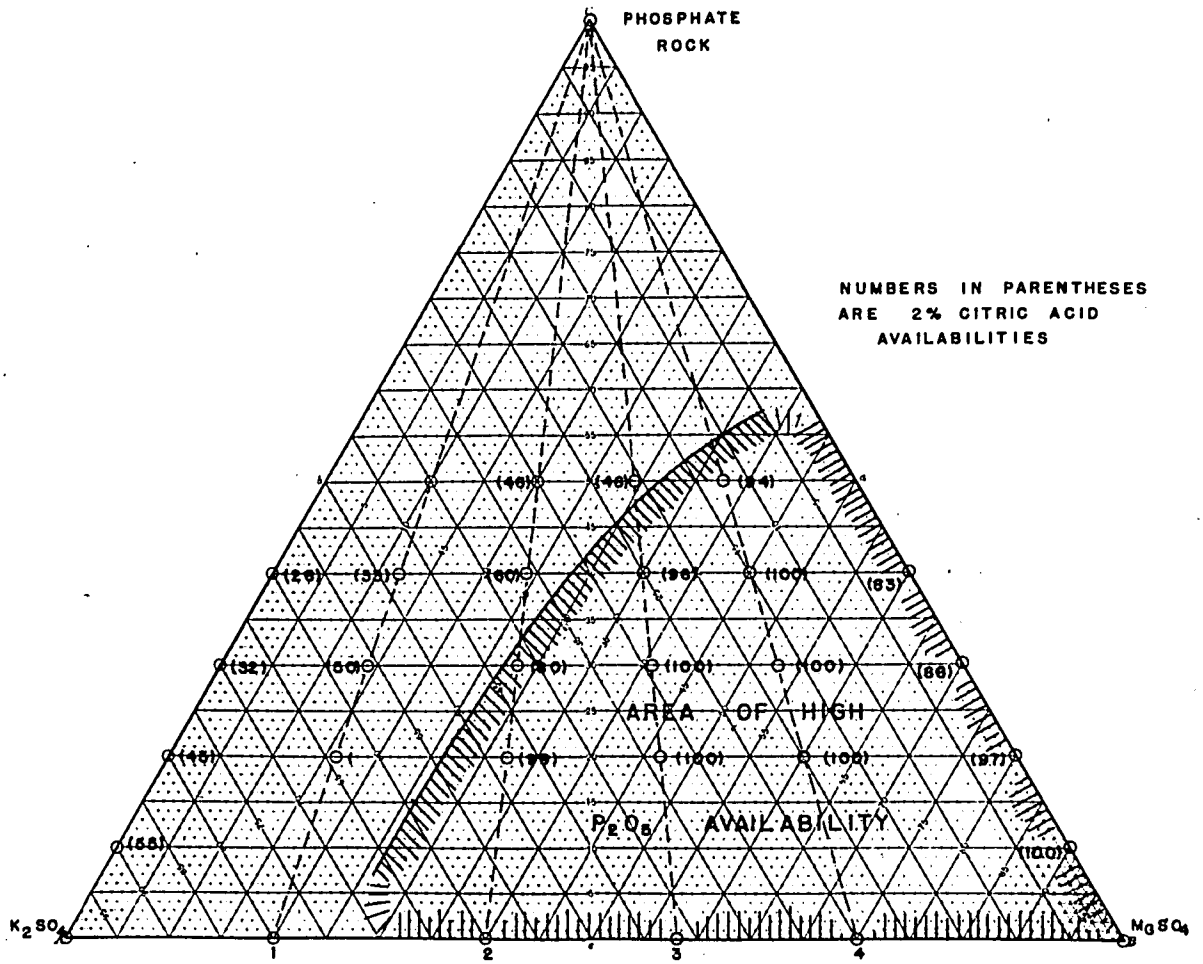


Figure 14. Effect of Composition on Availability of Fused Products from Mixtures of Phosphate Rock-$MgSO_4$-K_2SO_4

Table 8. Results of Fusion Studies of the Three Component System, Magnesium Sulfate - Potassium Sulfate - Phosphate Rock

Fusion	Original Composition			Product Composition (%)			Calc. Total P_2O_5	% Availability	
	$MgSO_4$	K_2SO_4	Rock	Citric P_2O_5	Citrate P_2O_5	Total P_2O_5		Citric Acid	Citrate Soluble
E-1	10	40	50	5.5	(Poor Fusion)		16.35		
I-1	10	40	50		(Poor Fusion)		16.35		
D-1	12	48	40	(Exploded)			13.08		
H-1	12	48	40	4.4	3.28	13.1	13.08	33	25
C-1	14	56	30		(Poor Fusion)		9.80		
G-1	14	56	30	4.0	3.04	7.8	9.80	50	38
B-1	16	64	20	(Exploded)			6.54		
F-1	16	64	20	(Exploded)			6.54		
E-2	20	30	50	5.6	2.6	12.0	16.35	46	22
I-2	20	30	50		(Poor Fusion)		16.35		
D-2	24	36	40	7.5	4.2	12.4	13.08	60	34
H-2	24	36	40	10.8	(Poor Fusion)		13.08		
C-2	28	42	30	8.21	7.76	10.3	9.80	80	75
G-2	28	42	30	8.5	6.96	10.3	9.80	82	68
B-2	32	48	20	7.9	7.6	8.0	6.54	99	95
F-2	32	48	20	7.4	7.2	7.9	6.54	93	91
E-3	29	21	50	(Lost Sample)			16.35		
I-3	29	21	50	7.75	6.88	16.8	16.35	46	41
D-3	34.8	25.2	40	13.3	13.3	13.8	13.08	96	96
H-3	34.8	25.2	40	13.2	13.5	13.6	13.08	97	99
C-3	40.6	29.4	30	11.9	11.8	11.2	9.80	100	100
G-3	40.6	29.4	30	10.4	10.3	10.6	9.80	98	97
B-3	46.4	33.6	20	7.4	7.5	7.4	6.54	100	100

I-2	20	30	50		(illegible)				
D-2	24	36	40	7.5	4.2	12.4	13.08	60	34
H-2	24	36	40	10.8	(Poor Fusion)		13.08		
C-2	28	42	30	8.21	7.76	10.3	9.80	80	75
G-2	28	42	30	8.5	6.96	10.3	9.80	82	68
B-2	32	48	20	7.9	7.6	8.0	6.54	99	95
F-2	32	48	20	7.4	7.2	7.9	6.54	93	91
E-3	29	21	50	(Lost Sample)			16.35		
I-3	29	21	50	7.75	6.88	16.8	16.35	46	41
D-3	34.8	25.2	40	13.3	13.3	13.8	13.08	96	96
H-3	34.8	25.2	40	13.2	13.5	13.6	13.08	97	99
C-3	40.6	29.4	30	11.9	11.8	11.2	9.80	100	100
G-3	40.6	29.4	30	10.4	10.3	10.6	9.80	98	97
B-3	46.4	33.6	20	7.4	7.5	7.4	6.54	100	100
F-3	46.4	33.6	20	7.0	7.0	7.2	6.54	97	97
E-4	37.5	12.5	50	16.9	16.5	17.0	16.35	99	97
I-4	37.5	12.5	50	16.6	(Poor Fusion)		16.35		
D-4	45	15	40	14.6	14.5	14.6	13.08	100	100
H-4	45	15	40	13.5	13.4	13.4	13.08	100	100
C-4	52.5	17.5	30	10.3	9.6	10.8	9.80	96	89
G-4	52.5	17.5	30	10.0	9.2	10.0	9.80	100	100
B-4	60	20	20	7.6	7.5	7.2	6.54	100	100
F-4	60	20	20	8.0	8.0	8.1	6.54	100	100

Compositions D-1, B-1, and F-1 exploded in much the same manner as the cryolite fusions. These explosions were quite forceful and shattered the glass beaker containing the quench water.

Compositions high in phosphate rock and low in magnesium were very difficult to fuse, giving poor melts and low availability. Compositions containing greater than 50 per cent rock could not readily be fused.

Compositions high in magnesium gave very fluid melts which showed high availability. In the area bounded by the curve and the $MgSO_4$ apex, product availabilities of 80 per cent or higher were obtained. This area is shown as the shaded portion of Figure 14. Compositions outside this area gave availabilities considerably less than 80 per cent and the availability decreased markedly as the phosphate rock content was increased.

Compositions on the tie line from the rock apex to base composition 3 are equivalent to mixtures of pure langbeinite and various amounts of phosphate rock. Along this tie line maximum P_2O_5 availability occurs at a minimum composition of 60 per cent base composition 3. In the langbeinite-rock fusions this occurred at 70 per cent langbeinite. When proper account is taken of the P_2O_5 impurity in the langbeinite used, the equivalent langbeinite composition would be approximately 65 per cent, which is in fair agreement with

the 60 per cent composition found in the three component studies.

The citric acid and citrate availabilities of Table 8 have been plotted as ordinate and abscissa in Figure 15 and a smooth curve drawn. A high degree of correlation is indicated, within the range studied, and availabilities greater than 95 per cent are shown to be approximately the same by either method.

Quenching media studies

Quenching studies were undertaken as a result of the solubility of potassium and magnesium in the quench water, as previously shown, to develop a method or media which would be applicable to pilot plant or commercial processes in which dissolution would not occur. Various methods or media were tried, including steam, air, carbon tetrachloride and saturated sulfate solutions. The results of these studies are given in Table 9.

Air and steam quenching were tried in the apparatus shown diagrammatically in Figure 16. A flat spray was obtained by making a triangular nozzle on the end of the copper inlet pipe. The melt was poured into the tee and was carried through the pipe by the spray and discharged into a 1000 ml. beaker at the other end. Neither air nor steam proved satisfactory as a quenching medium. The melt was not

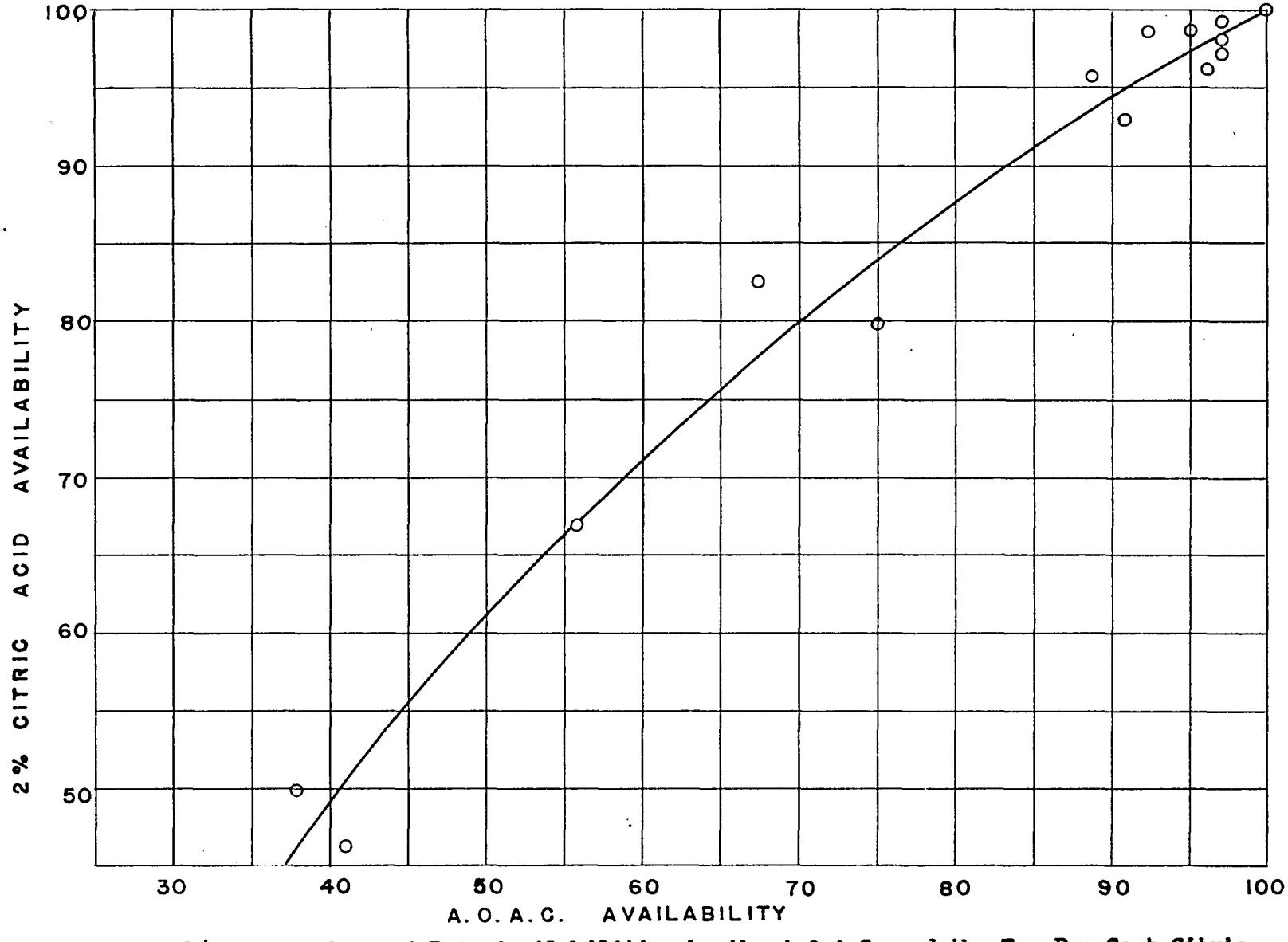


Figure 15. Comparison of P_2O_5 Availabilities by the A.O.A.C. and the Two Per Cent Citric Acid Methods

Table 9. Composition of Fusions of Phosphate Rock and Langbeinite Quenched in Various Media

Fusion	Langbeinite (%)	Quench	Product Composition		Availability (% of Total)
			Total	Available	
Q_1	70	Steam	14.5	12.0	83
Q_2	70	"	14.6	11.2	78
Q_3	70	CCl_4	14.5	13.6[a]	92
Q_4	70	K_2SO_4[b]	14.5	14.1	97
Q_5	70	K_2SO_4[b]	14.5	14.4	99
2-6-a	50	K_2SO_4 & $MgSO_4$[b]	19.1	5.2	27
2-6-b	50	"	19.6	7.0	36
2-5-a	60	"	16.4	15.1	92
2-5-b	60	"	16.4	15.1	92
2-4-a	60	"	16.0	15.0	94
2-4-b	60	"	15.9	15.0	94
2-3-a	65	"	14.7	13.7	94
2-3-b	65	"	14.7	13.7	94
2-2-a	68	"	13.9	12.9	93
2-2-b	68	"	13.9	13.0	94
2-1-a	70	"	12.4	12.0	96
2-1-b	70	"	12.8	12.1	95

[a]Analysis of smallest particles. Large particles were not quenched by the liquid.

[b]Saturated solution.

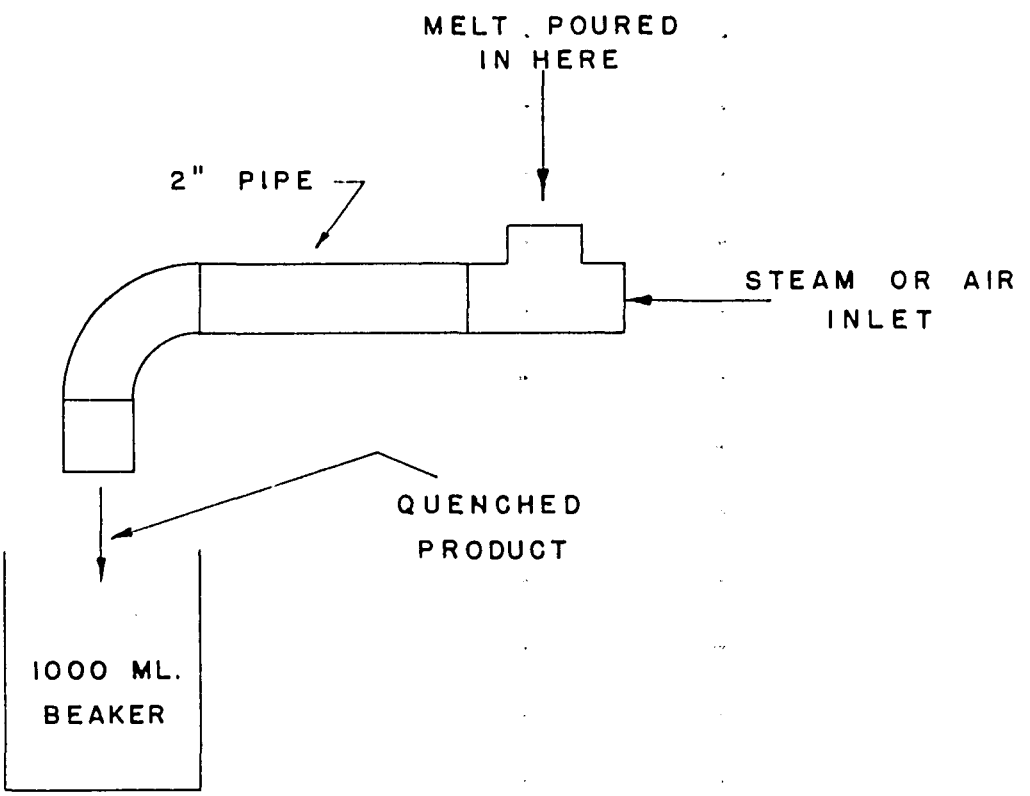


Figure 16. Diagrammatic Sketch of Apparatus for Air and Steam Quenching

completely broken up by the spray and large lumps were carried through the apparatus into the beaker where they cooled very slowly. Considerable difficulty was experienced with condensate when steam was used. The steam available was of poor quality and considerable water was always deposited in the beaker. An electric resistance heater and a condensate leg were installed on the steam inlet line but little improvement was obtained.

Quenching in carbon tetrachloride was also not satisfactory. There was no granulation or shattering of the melt, rather the whole molten mass sank to the bottom of the beaker and cooled slowly. This behavior could be expected also in other organic solvents of low specific heat.

To preserve the "shock" quenching action of water and still prevent dissolution of potassium or magnesium, saturated solutions of K_2SO_4 and $MgSO_4$ were tried for quenching the melt. A saturated K_2SO_4 solution was used first to determine the effect of a salt quench, with respect to P_2O_5 and K_2O solubilities, upon fusions made with the previously determined optimum compositions of 70 per cent langbeinite and 30 per cent phosphate rock. These tests gave good quenching action and the P_2O_5 availability remained essentially the same as with distilled water quenching. The product composition in respect to potassium increased, however, from 11.5 per cent to 13.0 per cent K_2O. Analysis of

the quench water, before and after quenching, showed no appreciable change.

A series of fusions was therefore made using a quench solution saturated with respect to K_2SO_4 and $MgSO_4$ in which compositions of the original charge were varied from 50 to 70 per cent. The results, in terms of P_2O_5 solubility, are given in Table 9.

Product evaluation

Aqueous quenching of the melts shattered the product into small fragments having the appearance of oatmeal. After drying, the product was chalk white and quite soft. It was ground to minus 80 mesh, dried for five hours at 100° C. and analyzed for total P_2O_5, available P_2O_5, K_2O, MgO, and fluorine according to methods previously described.

The value of a product as a phosphatic fertilizer is based on its P_2O_5 availability, expressed as per cent available P_2O_5 divided by the per cent total P_2O_5. In this respect availability refers to the solubility of the P_2O_5 in a prescribed solvent, either 2 per cent citric acid or neutral ammonium citrate. The availability of K_2O and MgO has the same meaning except the solvent is hot water.

An advantage of the phosphate rock-langbeinite product over other fertilizers is that it contains in an available form two primary nutrients, phosphorous and potash, and

three secondary nutrients, sulfur, calcium, and magnesium. The fusion products from compositions containing phosphate rock and a minimum of 70 per cent langbeinite "A" were at least 97 per cent available with respect to P_2O_5 and MgO, and 95 per cent available with respect to K_2O.

As recently reported (17) East German chemists and fertilizer manufacturers are adopting the policy of incorporating magnesium sulfate in fertilizer. Their view is that many crop disorders -- particularly those of a cholorotic nature -- which have been attributed to soil acidity, are, in fact, symptoms of magnesium deficiency. When it is considered that magnesium is a dominant member of every molecule of chlorophyll, the case for extension of the NPK triangle is not weak. The phosphate rock-langbeinite product might then be designated as a 0-14-13-12 fertilizer.

Another advantage of the product is that it would not cause bag rot since it contains no free acid. The dried product does not require further curing and is non-caking. In commercial quantities it could be bagged and shipped directly from process.

X-ray patterns of some of the langbeinite-phosphate products were made by the Ames laboratory of the Atomic Energy Commission. They are presented in Appendix B.

PILOT PLANT INVESTIGATION

The results of the laboratory work on the langbeinite-phosphate rock fusion process were considered promising and therefore pilot plant studies were undertaken with the following objectives:

1. To demonstrate the feasibility of the process on a larger scale.

2. To determine suitable materials of construction for the fusion furnace.

3. To provide process data for commercial-scale plant design.

4. To provide data for accurate assessment of costs and economics.

5. To provide quantities of fused product for agronomic tests and for uniform specification analysis.

Materials and Procedure

Materials

The rock phosphate used in the initial pilot plant operation was Florida land pebble, designated as "G", purchased already ground from the Davison Chemical Company at Perry,

Iowa. In the later operation of the pilot plant unground Florida land pebble phosphate rock designated as "P" purchased from International Minerals and Chemical Corporation, Mulberry, Florida, was used. The screen analyses and chemical composition of these rocks are given in Tables 10 and 11, respectively.

Table 10. Screen Analyses of Raw Materials Used in the Pilot Plant

Screen Mesh	Per Cent of Sample		
	Ground Pebble Rock "G"	Unground Pebble Rock "P"	Langbeinite "B"
+ 3	--	2.1	--
- 3 + 8	--	14.1	12.1
- 8 + 14	--	37.8	29.8
- 14 + 28	4.5	22.1	26.2
- 28 + 48	9.5	9.0	15.8
- 48 + 100	10.1	8.0	8.9
-100 + 200	31.5	4.6	4.4
-200	44.4	2.3	2.8

The langbeinite used in the pilot plant tests designated as "B" was obtained from the Potash division of International Minerals and Chemical Corporation, Carlsbad, New Mexico (by way of its Mason City, Iowa plant), and its screen analysis and chemical composition are also given in Tables 10 and 11, respectively.

Table 11. Chemical Composition of Raw Materials Used in Pilot Plant

Constituent	Per Cent (Dry Basis)		
	Ground Pebble Rock "G"	Unground Pebble Rock "P"	Langbeinite "B"
P_2O_5 (total)	33.6	30.7	0.75
F	4.8	4.4	--
CaO	48.8	43.9	--
K_2O	--	--	22.1
MgO	.42	.30	18.9

Analyses

The raw material and product analyses for the pilot plant were made in accordance with the A.O.A.C. Method of Analysis (2) for total and available P_2O_5, K_2O and MgO. Fluorine was determined by the method of Brabson, Smith and Darrow (6) as set forth in the laboratory investigation studies.

Flue gas analyses were made for carbon dioxide, carbon monoxide, and oxygen by means of a standard Orsat apparatus. Dust in the flue gas was analyzed for total solids by the impinger method of Greenberg and Bloomfield (21) using a Fisher impinger tube and dust collecting tube.

A 1/2 inch O.D. copper tube for dust sample collection was bent with a three inch radius to form a probe four inches

long. The probe was inserted in the center of the exit gas flue with the open end directed upstream. The extension of the probe came out through the gas flue and was connected by rubber tubing to the impinger tube. The outlet of the impinger tube was connected to a wet test meter for flow measurement and an air ejector connected to the meter which was used to draw the sample from the exit pipe into the sampling tube and then through the meter.

The dust sampling procedure was as follows: The sampling lines were first purged. The sampling rate was then adjusted to one cubic foot per minute. One hundred and twenty-five milliliters of distilled water were placed in impinger and collecting tube, and approximately 10 cubic feet of sample were bubbled through the impinger. The time was recorded. The collecting tube and impinger were removed from the sample lines and the contents washed into an evaporating dish. Total solids obtained upon evaporation were expressed in terms of concentration in the flue gas sample and related to total dust loss by the total quantity of exit gas. The solids were subsequently analyzed for P_2O_5 and fluorine by methods already outlined.

Fluorine in the flue gas was determined as follows. One hundred milliliters of distilled water were placed in an impinger assembly like that used for the dust sampling and made alkaline by sodium hydroxide. A gas sample (not exceeding

1.0 cu. ft.) was taken from the exit flue at a rate of approximately one cubic foot per minute by means of the air ejector and bubbled through the solution in the impinger, the total quantity of gas sample being measured by the wet test meter.

The impinger assembly was removed and the contents washed into a 500 cc. volumetric flask and made to the mark. An aliquot was taken and titrated according to the method previously described for fluorine.

Pilot plant design and construction

A pilot plant was built having a capacity of one to two tons of product per day. The plant consisted essentially of a vertical shaft furnace, using natural gas as a fuel, a re-circulating quenching system and an agglomeration system for feed preparation.

The choice of the type and size of furnace was based on the following factors:

1. The furnace should be capable of operating at temperatures of at least 2500° F. and have good thermal efficiency.

2. The refractories used in contact with the melt should withstand its corrosive action at the temperatures employed.

3. The furnace should be capable of being fed continuously, or semi-continuously, and the molten product should be easily tapped.

4. Natural gas firing should be used, if possible, since this fuel is generally the most economical.

5. The furnace should be large enough to be representative of industrial practices in design and should be readily adaptable to commercial sizes.

6. The capacity of the furnace should be large enough to provide data outlined in the introduction to this section and yet be small enough as not to require extensive material handling.

Various types of furnaces have been tried for defluorination of phosphate rock by fusion. Curtis, et al. (13) describes tests on (a) a Detroit rocking indirect-arc electric furnace, (b) a rotary kiln, oil-fired, (c) a horizontal tilting converter furnace, also oil-fired, and (d) a regenerative oil-fired hearth furnace. Most of these had proved unsuccessful because of low thermal efficiency, short furnace life, or mechanical difficulties. Hignett and Hubbuch (27) investigated the use of an oil-fired vertical shaft furnace, with considerable success. Walthall and Bridger (64) used a direct-arc electric furnace for fusing phosphate rock and olivine and two commercial plants have

since been built using this type of furnace.

The electric arc type of furnace is limited to regions of low power costs and would not be applicable to Iowa or other Midwestern states. In addition the high temperatures of an electric furnace are not required for the langbeinite-phosphate rock process. A fuel-fired vertical shaft furnace with countercurrent movement of ascending hot gases and descending charge would favor relatively high thermal efficiency and this type was chosen for the pilot plant. Calculations were made of the heat release and combustion volume of the various furnaces reported in the literature and a furnace designed from these data to produce from one to two tons of fused product per day.

Figure 17 is a flow sheet of the process. The raw materials were received by truck in 100 pound paper bags which were emptied into wooden storage bins, each holding approximately two tons. The materials were discharged through side outlets in the bins, weighed in the desired proportions on a platform scale and mixed in a cement mixer. The mixed material was agglomerated in a rotary drum by addition of moisture, and the product screened to separate the fines. The undersized material was manually recycled to the rotary drum; the oversized was dumped on the floor to air dry. After air drying, the agglomerated feed was weighed and elevated in buckets to the top of the furnace and dumped

VE
FU

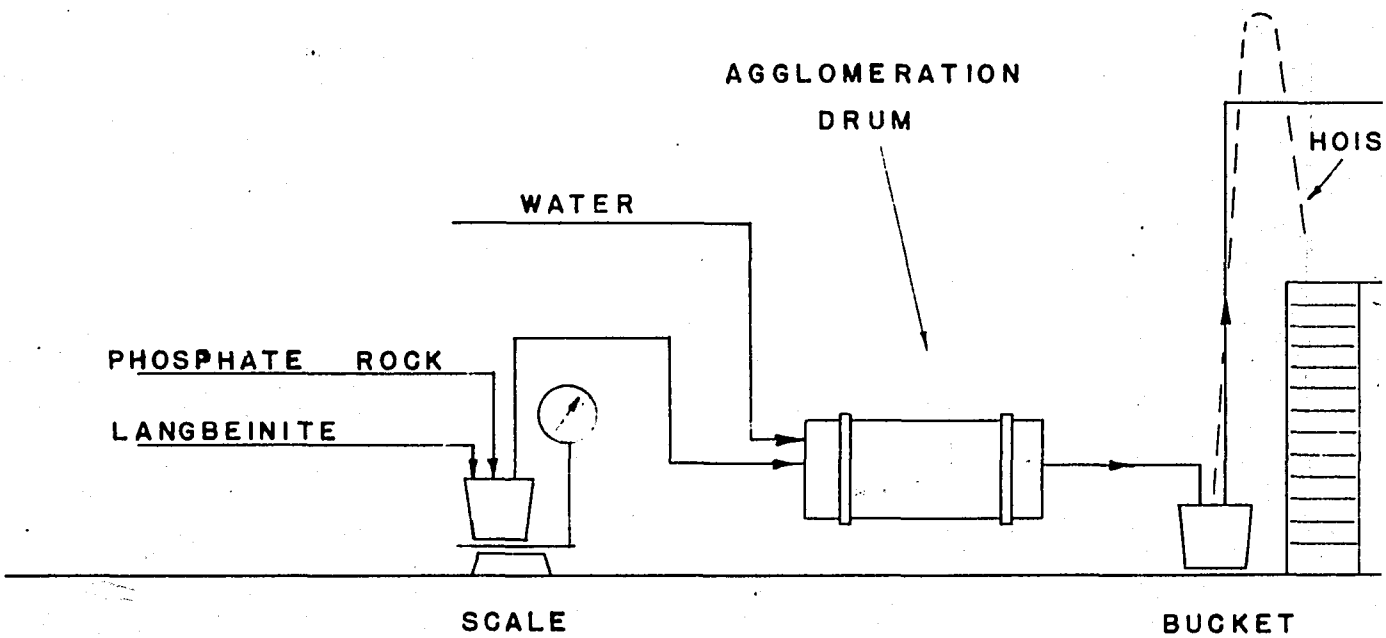
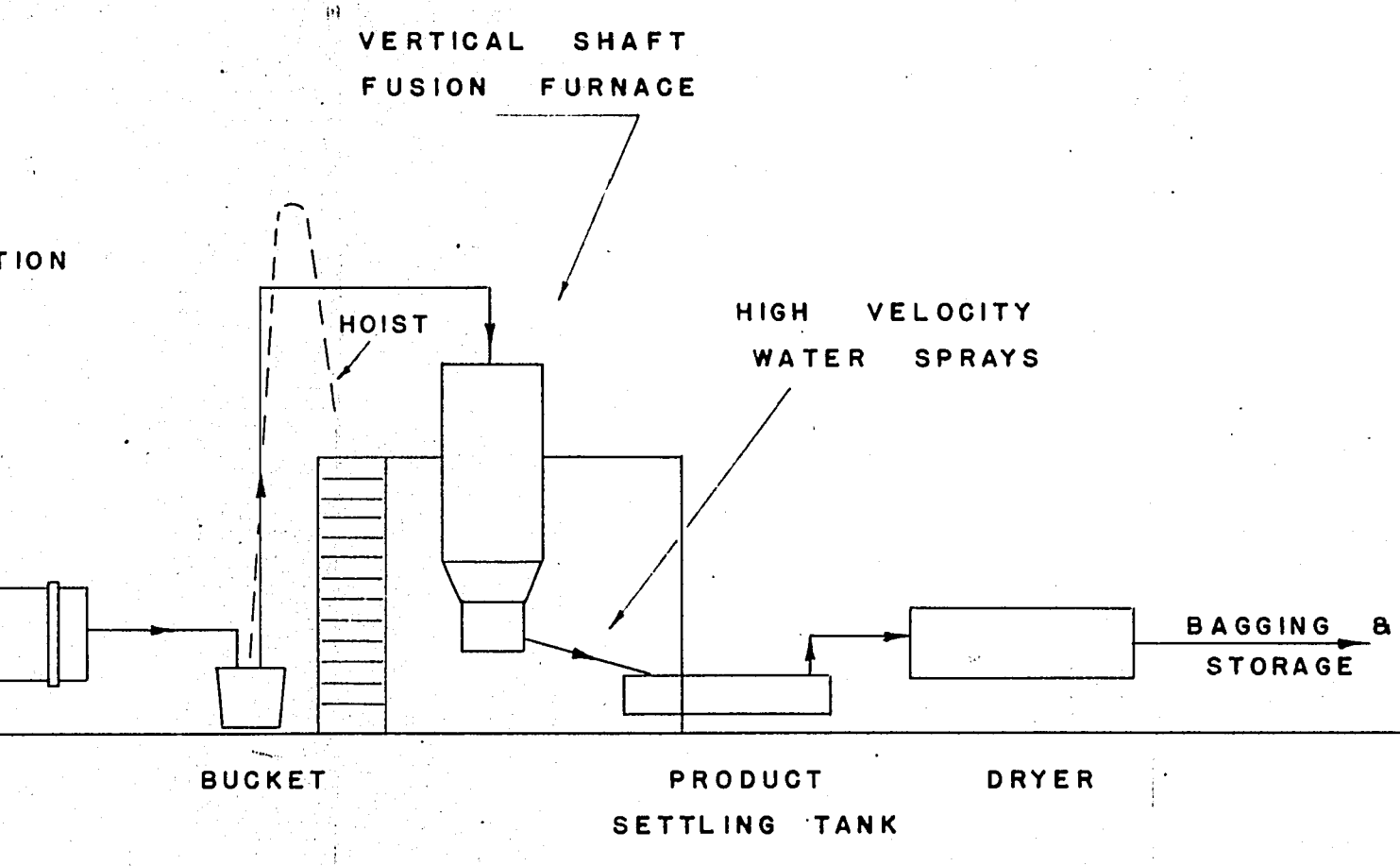


FIGURE 17. PILOT PL



7. PILOT PLANT FLOW SHEET

into the feed hopper. It was introduced into the furnace as required. The molten product from the furnace was quenched in a high velocity stream of saturated aqueous langbeinite solution. The quenched product was discharged from the quenching trough into a settling tank where the product settled out and the quenching water was recirculated to the spray nozzle at the furnace. The product was removed manually from the settling tank and allowed to drain in a pile. After dewatering by draining the product was dried in a small Link Belt Roto-Louvre drier. Dried product was weighed and bagged in 100 pound paper bags.

An assembly drawing of the furnace as designed and built is shown in Figure 18. The steel shell was made in sections and flanged together to facilitate access to the lining for repairs. The lining in the upper sections was A. P. Green fireclay brick backed by 1 1/2 inches of Plibrico Plisulate insulation, an asbestos-mineral wool product. The hearth and bottom sections were lined with six inches of Laclede chrome-plastic, having a fusion point above 3500° F.

Copper cooling coils were placed adjacent to the steel shell in the hearth section and burner nozzle as shown in Figure 19. Cooling coils were also installed adjacent to the steel shells in the lower portion of the straight section just above the hearth. The purpose of these coils was

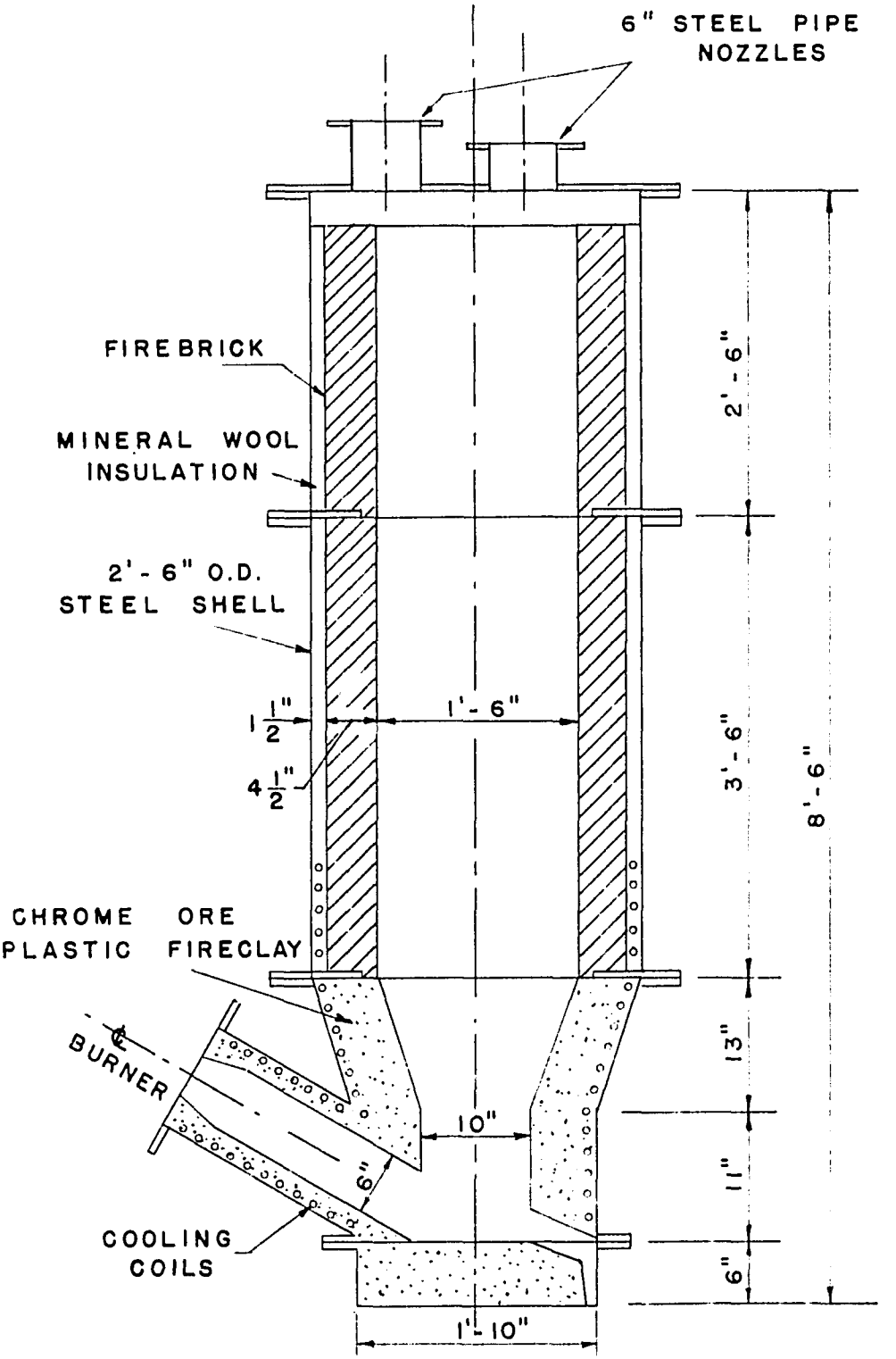


Figure 18. Assembly Drawing of Pilot Plant Furnace

Figure 19. Pilot Plant Furnace Hearth Showing Cooling Coils

two-fold: (1) to protect the steel, and (2) to counteract the corrosion of the lining by "freezing" a layer of melt on the surface of the lining. The TVA defluorination furnace described by Hignett and Hubbuch (27) had water sprays on the steel shell exterior, but this was considered unnecessary for the pilot plant furnace.

The upper sections of the furnace were supported by a structural steel frame as shown in Figure 20. In these sections, the brick lining was supported by an extension of the bottom flange of each section and the insulation was packed in the space between the brick and the steel. The mortar used for the firebrick was Plibrico "Demon" airset cement, an all-purpose fire clay cement.

After lining the hearth section, it was raised and bolted into position and the cooling coils connected to the water system. Thermometers were provided on the inlet and outlet of the coils and the discharge of each coil was so arranged that measurements of flowrates could be taken.

The feed hopper and flue outlet at the top of the furnace are shown in Figure 21. The flue extended outside the building and up through a steam jet ejector to an elevation 10 feet above the roof. The ejector was installed for control of the furnace draft with various charge levels. Also shown in this photograph, at the upper right, is the flue gas sampling and analysis equipment, consisting of a wet test

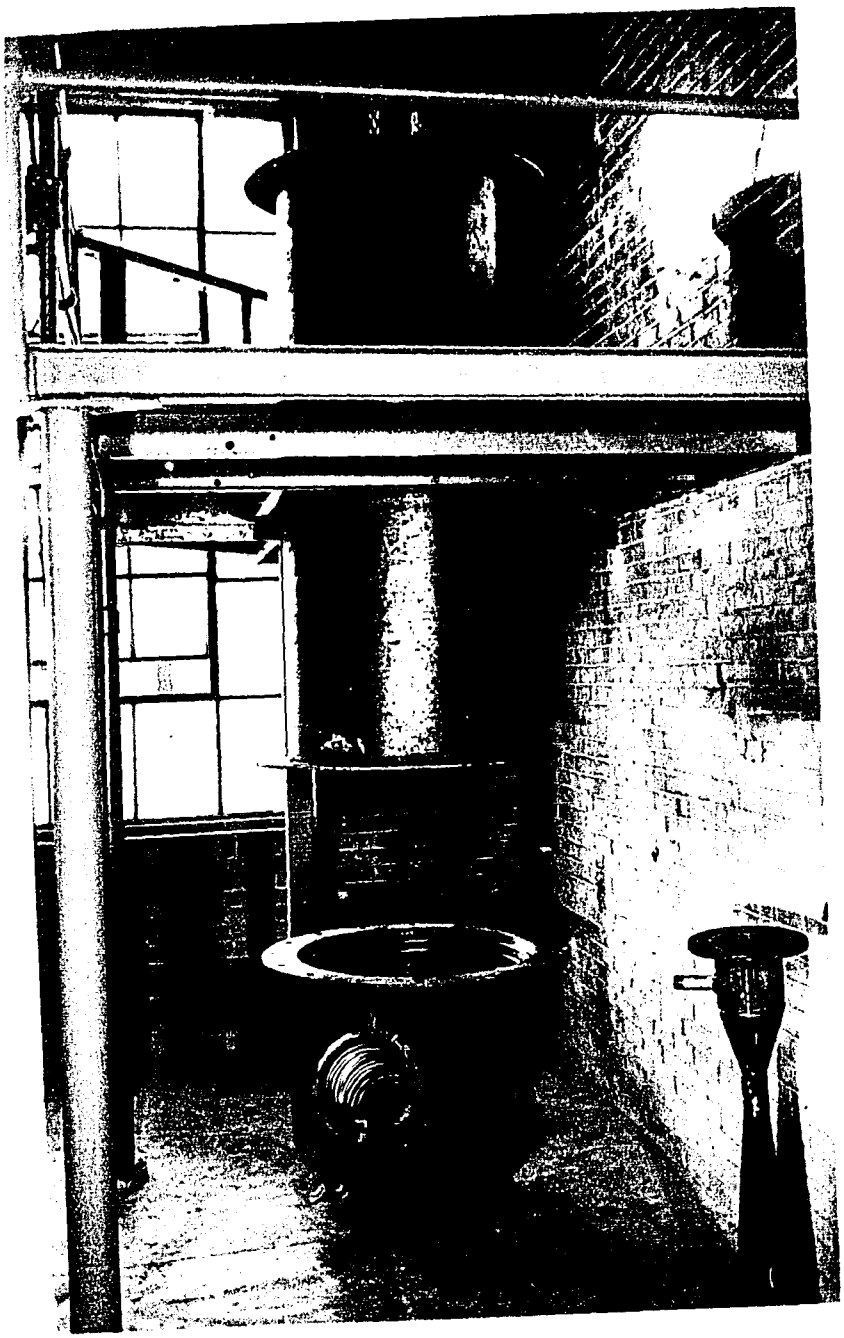


Figure 20. Pilot Plant Furnace Steel Shell and Supports

Figure 21. Pilot Plant Furnace Erected Showing Flue Gas Outlet and Sampling Apparatus

meter, an Orsat apparatus, and dust samplers. An air ejector was provided for pulling the flue gas sample through the various pieces of apparatus for analysis.

The burner and furnace controls are shown in Figure 22. A Hauck No. 781 combination proportioning oil-gas burner was used, purchased from Keating Coal Company, Des Moines, Iowa. This burner has a maximum capacity of 800 to 1000 cu. ft. of gas per hour. The manometers shown in the photograph indicate pressures at the following points:

1. Top of furnace in duct to stack
2. Draft just inside the burner port
3. Gas pressure at burner
4. Primary air pressure at burner

The horizontal manometer is a differential flow manometer connected to a pitot tube in the primary air line to the burner. Also shown (extreme left manometer) is a differential manometer connected to an orifice in the steam line leading to the steam jet ejector on the exit gas flue.

The furnace tapping spout and quenching system is shown in Figure 23. The quenching system consists of a spray head and discharge trough, product settling tank (foreground) and recirculating pump and piping. The spray head has 37-1/8 inch holes and the quench water is recirculated at 65 gallons per minute at 60 feet head by a Yeomans centrifugal pump S.O. 22796. The product was removed from the settling tank by a

Figure 22. Lower Section of Pilot Plant Furnace Showing Burner and Controls

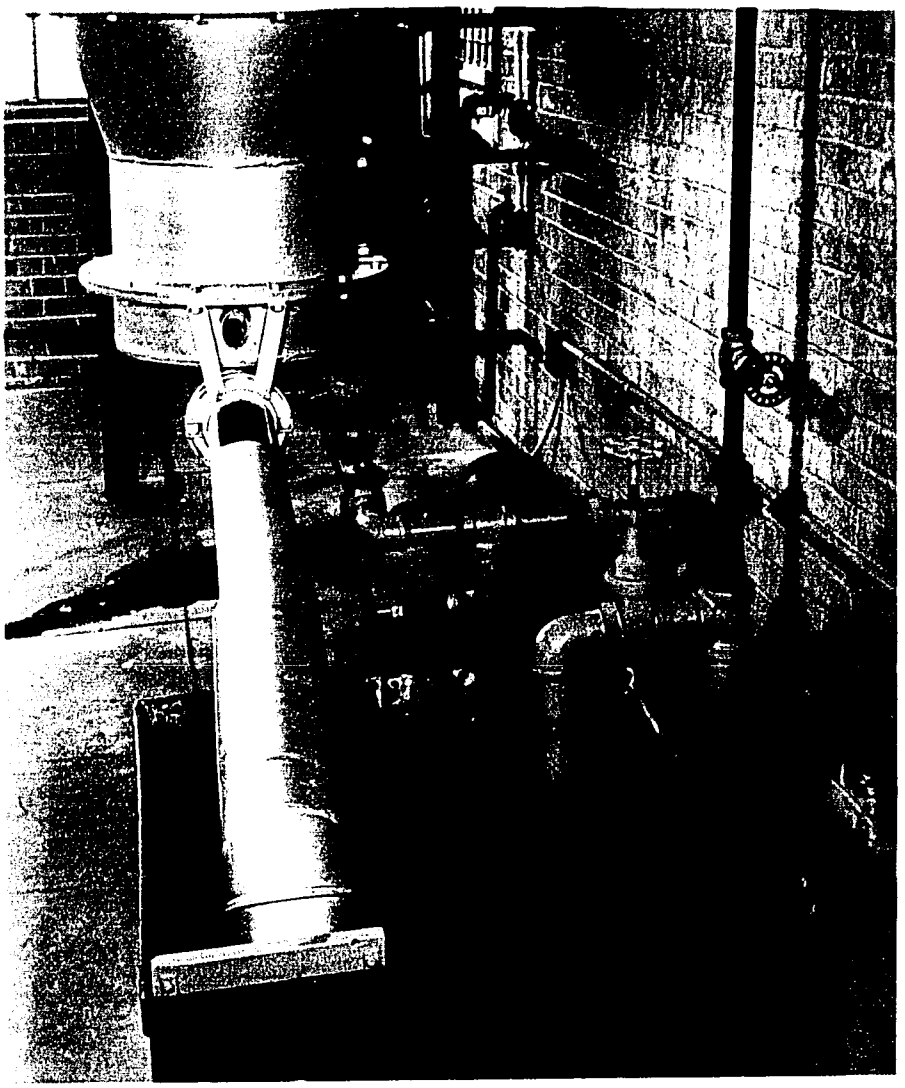


Figure 23. Pilot Plant Quenching and Recirculation System

wire screen basket and allowed to drain in a pile before drying and bagging.

The tapping spout shown in Figure 24 was enlarged after the photograph was taken. The reasons for this are discussed in a subsequent section.

The complete pilot plant, not including feed preparation equipment, is shown in Figure 25. The primary air blower is shown on the platform just to the left of the furnace.

Furnace feed preparation

Furnace feed was prepared by agglomerating the mixed phosphate rock and langbeinite into pellets from 3/8 to 3/4 inch in diameter. This was accomplished by tumbling in a 55 gallon steel drum with the ends removed as shown in Figure 26. The agglomeration step would not be necessary if raw materials of proper size could be obtained. However, mixed pellets of fine materials obtained by agglomeration would probably have a decided advantage in being easier to fuse.

The agglomeration procedure was as follows: The desired proportions of langbeinite "B" and phosphate rock were weighed on a platform scale in batches of 60 to 100 pounds. The materials were mixed dry in a motor driven cement mixer for about five minutes to insure uniformity. This mix was introduced into the rotary drum as required. The moisture content of the mass in the rotating drum was

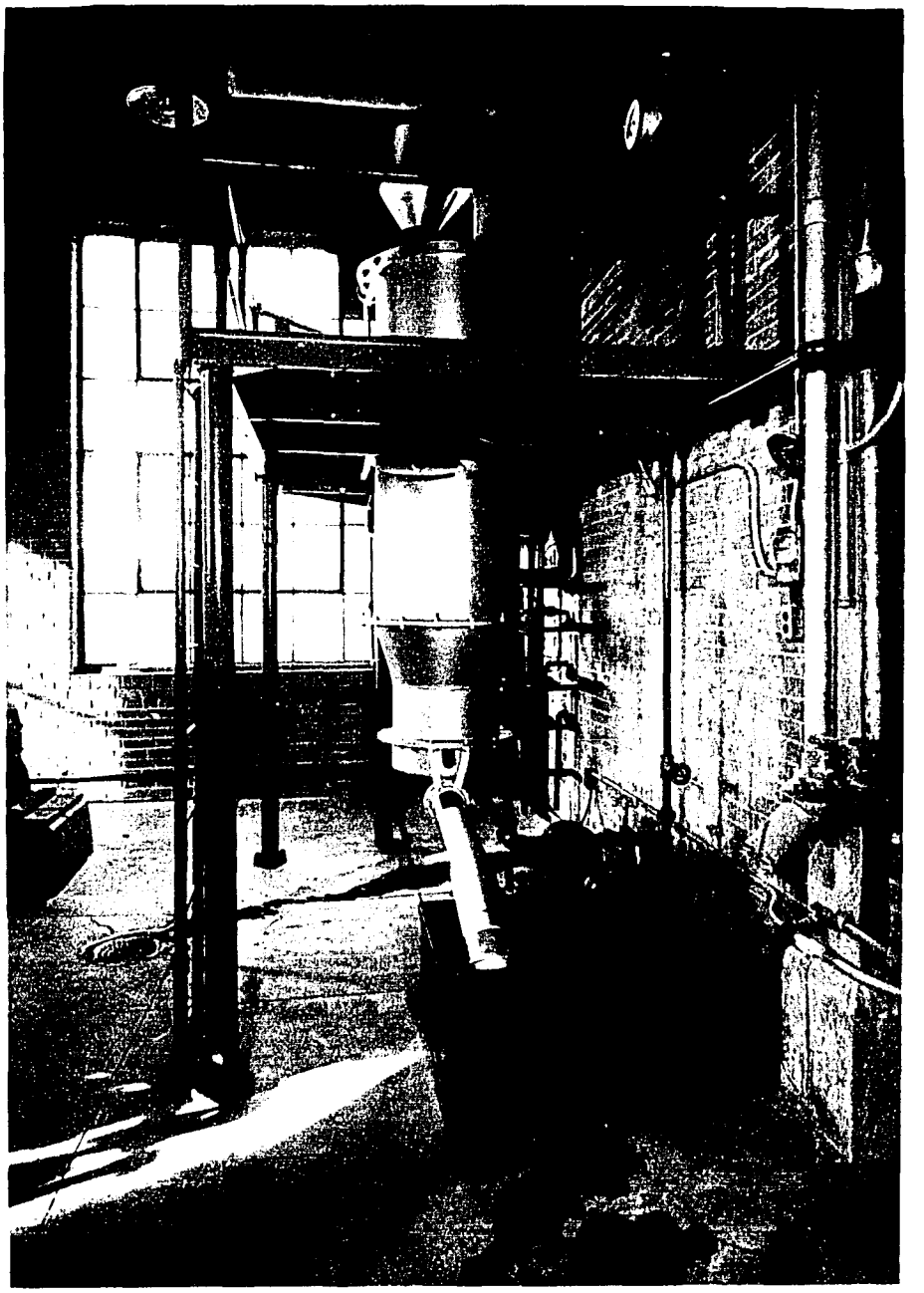


Figure 24. Completed Pilot Plant - End View

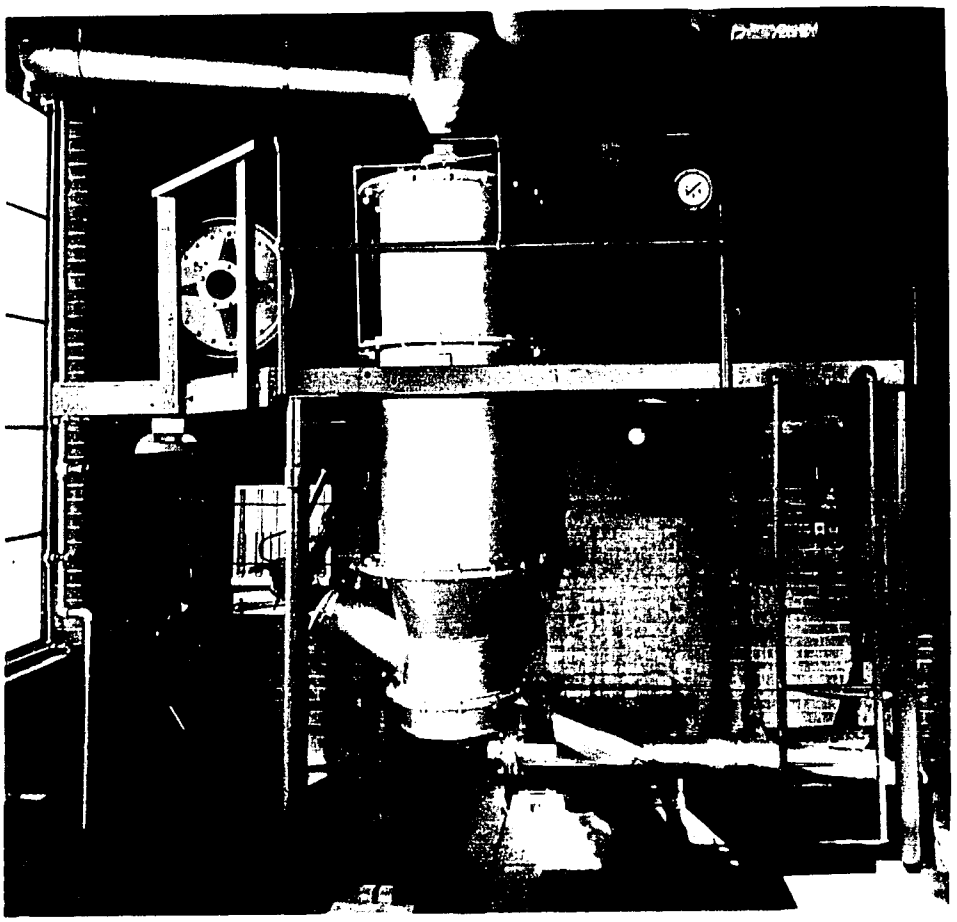


Figure 25. Completed Pilot Plant - Side View

Figure 26. Feed Preparation Equipment Showing Mixer and Agglomerating Drum

adjusted by addition of water and additional small amounts of the dry mixture were added until the material rolled into balls from 1/8 to 1/2 inch in diameter. The balls were discharged from the end of the drum and screened by hand. Material under 3/8 inch was recycled to the tumbler. This recycle proved quite laborious since the overall yield was about 20 per cent. The product from the operation, everything over 3/8 inch, was piled on the floor and allowed to air dry.

The critical part of the agglomeration was the moisture content of the material in the drum. Too much moisture caused the formation of just a few large balls, too little moisture caused a large number of small balls to be formed. At a moisture content of approximately 8 per cent, the balls formed rather uniformly in the size range plus 3/8 inch and minus one inch. The balls were round, quite firm and after drying were extremely hard. They withstood heating up to the melting point without disintegrating. One hundred pounds of agglomerated feed could be produced per hour.

Subsequent to the initial agglomeration, another 55 gallon drum was added to the tumbler to cut down the recycle required. A 1/2 inch mesh screen was also added to the discharge end which acted as a trommel and automatically screened the product.

Using the above procedure, two furnace feeds were prepared. The composition and P_2O_5 analysis of each is given in the following table:

Composition	Per Cent	
	I	II
Langbeinite "B"	65	68
Phosphate Rock "G"	35	--
Phosphate Rock "P"	--	29
Bentonite	--	3
P_2O_5	11.9	9.0

Furnace feed I was prepared with a 65 to 35 weight ratio of langbeinite "B" to phosphate rock after laboratory fusions of agglomerated feed of this composition indicated that high availability could be obtained. Following initial operation of the pilot plant with this feed, furnace feed II was prepared, with the langbeinite ratio increased in an effort to obtain higher P_2O_5 availability in the product.

Agglomeration of furnace feed I was readily obtained when the proper moisture was added, since the phosphate rock provided sufficient fines to cement the particles together. The pebble rock "P" used for furnace feed II did not have sufficient fines, however, and up to 3 per cent bentonite had to be added.

Operating procedure

The furnace was initially filled to the desired charge depth with agglomerated feed, introduced through the charging hopper at the top of the furnace. Approximately 800 pounds of feed were required to fill the furnace to the maximum depth of 8 feet. For the experimental runs, however, charge depths of from 2 to 5 feet were maintained, equivalent to an initial charge of from 120 to 520 pounds.

After charging, the furnace was warmed up for a period of two to four hours at a low heating rate (50 to 100 cubic feet of natural gas[1] per hour). During this period the furnace controls were adjusted and initial readings taken. A slight minus pressure (0.1 centimeter of water) was maintained at the burner by means of the steam jet ejector in the furnace gas exit flue. It was necessary to thoroughly purge the steam line of condensate before using the jet ejector because of the possibility of condensate draining back through the exit flue into the furnace. The precaution of purging the gas line before lighting the burner was also necessary for personnel safety.

Following the initial warming up period of eight hours the gas rate was gradually increased over a period of one hour to 200 to 300 cubic feet per hour. At this rate the

[1]Ames city gas. Heating value = 994 Btu/cu.ft.

hearth temperature was about 2000° F. and the charge began to melt. As the melting occurred the gas rate was increased to the desired maximum (350 to 450 cubic feet per hour). The hearth temperature at this gas rate was 2400 to 2600° F. and melting took place quite rapidly.

The melt was either tapped intermittently or run out continuously. Intermittent tapping proved to be difficult to achieve and continuous operation was used in the later runs. The molten product stream from either method of tapping was broken up by high velocity water jets and discharged through a pipe into a settling tank. The quench water was previously saturated with langbeinite to prevent dissolution of potassium and magnesium from the melt. It was recirculated from the settling tank to the water jets. Product was removed from the settling tank by means of a screen wire basket and dumped in a pile for drainage of surface water.

During the melting process a positive pressure of one to two centimeters of water was maintained just inside the burner port. This was obtained by increasing the primary air and properly adjusting the draft by means of the air ejector. When the product was being tapped continuously a flame about six inches long was maintained at the tapping hole. This kept the outlet hot and prevented freezing of the melt.

The charge settled in the furnace during operation and feed was added intermittently to keep a constant charge depth.

Temperatures, pressures, and flow rates were taken every hour during each run. Flue gas samples for fluorine, dust, and Orsat analyses were taken less frequently.

Product handling and drying

The product from the quenching operation was finely granulated, ranging in size from very fine sand to a maximum size of 1/8 inch. During extended runs on the pilot plant the product was dumped into a wooden bin for draining. It tended to set up when wet and was taken out of the bin and spread out on the floor to air dry. An area large enough to get complete drying was not available, however, and this method of drying proved unsatisfactory. Subsequently a small Link-Belt Roto Louvre drier, part of another pilot plant in the Chemical Engineering Department, was tried. Results were satisfactory. The drier was heated for about one hour and the wet product introduced by means of the belt feeder. A bed of material was maintained in the drier approximately four inches deep by means of retainer rings in the drier outlet. The burner was run fully open and the inlet gas was about 560° F. The product temperature, however, never exceeded 180° F. The dried product was packaged directly into

100 pound paper bags. A drying rate of about two pounds per minute could be maintained.

Experimental Results

Ten experimental pilot plant runs were made and two types of feed, prepared as stated earlier, were tested. Total operating time of the furnace was 105 hours. A summary of the important data for these runs is given in Table 12 and the major observations are presented in the following pages.

The initial operation of the pilot plant was made using the feed designated as I in the table on page 91. This feed was easy to handle and could be dropped into the furnace from the charging hopper without disintegration. At a hearth temperature of 2400° F. a pool of melt could be obtained in 5 to 10 minutes. Intermittent tapping of the melt was used for Runs I through VI. Continuous tapping was used for the subsequent runs.

It was demonstrated that intermittent tapping was possible and that good product could be made. However, intermittent tapping was very difficult to maintain and was not practical for continued operation of the furnace, without some redesign of the hearth section.

Table 12. Summary of Data From Pilot Plant O

Run	Feed[a]	Charge Depth (ft.)	Temperatures (° F.) Hearth	Exit Gas	Pressures (cm. H_2O) Burner	Exit Gas	Gas Rate[b] (cfh)	Length (h
I	I	5	1750	138	-0.5	-1.0	250	1
II	I	5	1800	263	-0.5	-1.0	100	1
III	I	5	--	--	--	--	--	1
IV	I	1	2300	800	-0.2	--	210	
V	I	2	--	--	0.0	+3.0	--	
VI	I	2	1900	330	0.2	+2.0	288	1
VII	I	5	2480	155	1.5	-3.0	402	1
VIII	I	5-3	2400	--	2.0	--	456	
IX	I	2	2400	191	1.5	-4.0	516	
X	II	$2\frac{1}{2}$	2600	172	0.0	-4.0	558	

a. see feed composition page 91
b. maximum
c. total operating time including warm up
d. intermittent tapping used on runs I through VI
continuous tapping used on runs VII through X
e. typical product samples
f. actual produ
g. "
h. "
i. "

able 12. Summary of Data From Pilot Plant Operation

Pressures (cm. H_2O) Burner	Exit Gas	Gas Rate[b] (cfh)	Length of Run[c] (hrs)	Weight of Product[d] (lbs.)	Product Composition[e] (%) Total P_2O_5	Avail P_2O_5	Availability (% of Total
-0.5	-1.0	250	18	-			-
-0.5	-1.0	100	17	--	13.9	9.0	65
--	--	--	10	--	14.0	13.8	99
-0.2	--	210	9	--	10.5	10.3	98
0.0	+3.0	--	9	21	12.4	10.5	85
0.2	+2.0	288	12	67	13.1	10.8	77
1.5	-3.0	402	12	1007[f]	12.4	9.9	80
2.0	--	456	8	404[g]	13.2	9.4	71
1.5	-4.0	516	5	315[h]	12.7	11.2	89
0.0	-4.0	558	5	477[i]	9.2	8.4	91

arm up
s I through VI
VII through X

f. actual production rate, 150 pounds per hour
g. " 125 "
h. " 150 "
i. " 120 "

Continuous tapping proved very successful with regard to operation. Good burner control was possible and a very fluid product stream could be maintained. Quality of the product was impaired, however, by the small holdup of the melt, resulting at times in incomplete fusion.

Runs I through III were made with a charge depth of five feet, equivalent to an initial charge of approximately 520 pounds. The furnace was operated with a draft at the burner for induction of secondary air. This proved difficult to control since the resistance of the charge to the flow of gases changed as melting took place, resulting in wide variations of the draft at the burner. Often the flame was pulled out and ignited in the hearth causing serious back-firing. Proper hearth temperatures were difficult to maintain under these conditions and melting sometimes took place in the upper part of the furnace. Unfamiliarity with the burner probably accounted for most of this trouble.

The major difficulty in these runs was getting the melt out of the furnace. A good melt could be obtained with proper burner control but in many cases it could not be tapped. The tap hole became plugged by unfused and partially fused charge and initial attempts to break through by rodding were unsuccessful. An oxy-acetylene torch and later an oxygen-steel pipe torch were tried. The latter consisted of

a steel pipe (1/4 inch) connected to an oxygen cylinder by means of a rubber hose. The end of the pipe was heated with an acetylene torch and the oxygen turned on. The steel pipe burned readily, releasing intense heat. The torch was inserted in the tap hole in an attempt to melt a hole through the plugged portion.

A good tap was made during Run III by a combination of tapping methods, but continued operation under these conditions was deemed inadvisable. The product was well fused, however, and was 99 per cent available with respect to P_2O_5.

Run IV was made to test various tapping procedures, using smaller charge depths. The charge remaining from the previous runs was removed and the hearth chipped clean of solidified melt. It was noted that the lining had not been attacked and withstood abrasion and chipping very well.

With the furnace clean the hearth was warmed up and about 25 pounds of charge added. Good burner control could be obtained resulting in a higher hearth temperature. The charge melted perfectly as could be seen through the sight glass in the top of the furnace. Tapping was easily accomplished by rodding and a product of 98 per cent availability was obtained.

Additional charges were added and melted in the same manner. Tapping became increasingly difficult, however, due to a build up around the tap hole. The build up was

apparently not penetrated by the heat and gradually increased. In attempting to raise the hearth temperature by increasing the gas rate, a higher draft was required and the flame was pulled up the furnace away from the outlet spout. This melted more charge but did not melt the solid portion around the tapping spout. The melt eventually filled the burner port opening and the furnace had to be shut down.

During the latter part of this run, none of the tapping methods proved effective. Heated rods, oxy-acetylene and oxy-pipe torches were tried to no avail.

Run V was made after modifying the tap hole. The original carbon lining, shown in Figure 27(a) was removed and the outlet enlarged to about 2½ inches in diameter. The hearth end of the tapping hole was closed with a fire clay plug, leaving a one inch tapping hole. This hole was plugged with a fireclay cone.

With a charge of 134 pounds the furnace was brought up to operating temperature and four taps were readily made by rodding through the small tapping hole. The fireclay plug at the hearth end of the tapping hole broke, however, and could not be replaced while the furnace was hot.

For Run VI the tap hole was again enlarged and tapered to fit a replaceable graphite block as shown in Figure 27(b). This block was about 1½ inches thick and had a one inch hole near the bottom. A carbon rod was tapered to fit this hole

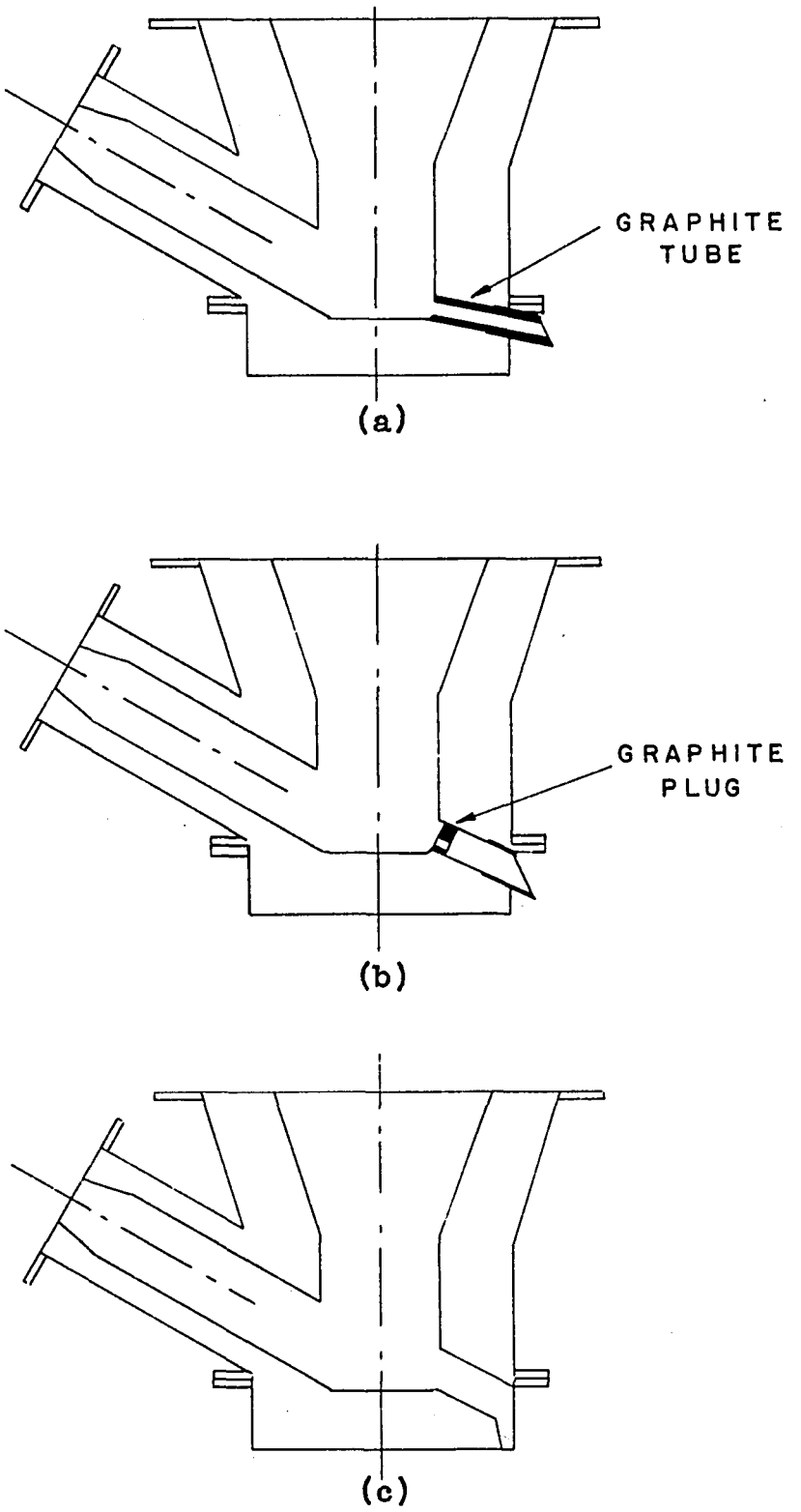


Figure 27. Details of Furnace Tapping Outlet

and was used as a plug. In addition, two laboratory blast burners were mounted to keep the outlet hot.

With this arrangement tapping was very simple and 11 taps (at intervals of 10 minutes) were made before the outlet plugged.

Run VII was started using the same tapping arrangement as in the previous run. An additional 364 pounds of charge were added making the charge height approximately five feet. The outlet became plugged, however, and tapping was impossible through the tapping hole. The plug was therefore broken up and removed, and the hearth and outlet rodded clean of solidified melt. The outlet was then left open and the burner adjusted so that a flame about six inches long emerged from the outlet. The melting rate was sufficient to provide a continuous product stream about 1/4 inch in diameter. The emerging flame kept the stream fluid and prevented solidification of the product in the outlet.

For the continuous tapping, a positive pressure of one to two centimeters of water was maintained at the burner. The length of the flame emerging from the outlet was adjusted by primary air control and draft regulation by the steam jet ejector. During this run continuous product tapping was maintained for eight hours, being interrupted only at times when the charge settled non-uniformly and filled the hearth with agglomerated feed. The production rate was approximately 150 pounds per hour.

The product was very finely granulated by the water sprays and appeared to be well quenched. After about an hour of continuous tapping, the quench water steamed profusely and gave off very pungent fumes. Typical analysis of the product showed a P_2O_5 availability of 80 per cent.

The laboratory work had shown that availability was a function primarily of composition, fusion conditions, and quenching. Since high availabilities had been obtained in Run III and IV with the same feed, it was felt that conditions of quenching or melting caused the low availability of the product from Run VII.

To test the effect of the fresh quench water, Run VIII was made using fresh water for the initial quenching and sewering the water after a period of one hour of recirculation. Samples were taken of the product before and after changing quench water but the analysis showed no significant difference in the P_2O_5 availability. The average availability of the product, for this run, was only 71 per cent which indicated that proper fusion was not being attained. This was evidenced by dark, unfused particles being carried out of the furnace by the molten stream. Sampling of the product may have included some of these unfused particles, consequently showing low availability. The production rate during this run was approximately 125 pounds per hour.

Either a longer fusion time or a higher fusion temperature was apparently required and Run IX was made to determine if the melt could be held in the molten state and tapped intermittently. Successful product taps were made at intervals of five and 10 minutes but the outlet soon became plugged and could not be tapped. The furnace had to be shut down to clean out the hearth and tapping outlet. Operation was subsequently resumed using continuous tapping. By careful burner control the temperature in the hearth was raised to 2500° F. and special samples, taken during good operation, analyzed as high as 95 per cent availability. Samples taken at random throughout the product had availabilities of 73 to 89 per cent.

Furnace feed II, page 91, was used for Run X to demonstrate that unground pebble phosphate rock could be successfully fused in agglomerated form with langbeinite. The outlet was again modified as shown in Figure 27c. With this feed, initial melting of the charge required a higher temperature than did Feed I but other operating conditions were approximately the same. Continuous tapping was used with the hearth under a slight positive pressure. The production rate was approximately 120 pounds per hour. Temperature in the hearth was 2500 to 2600° F.

At times during the run, unfused charge fell into the hearth and was carried out with the melt as was evidenced by

the appearance of dark particles in the product. Product samples taken during periods of good operation showed up to 92 per cent availability. Random samples taken throughout the product showed 72 to 89 per cent availability.

The better product from Runs IX and X were analyzed for fluorine, MgO, K_2O as well as P_2O_5. The analyses are shown in Table 13.

Table 13. Analysis of Typical Fused Product From Runs IX and X of the Pilot Plant

Run	IX	X
P_2O_5 - total	12.7	9.2
P_2O_5 - avail	11.2	8.4
P_2O_5 - availability	89	92
K_2O	12.9	12.5
MgO	12.0	11.0
F	1.64	1.6

Analyses of the exit gas, taken at approximately the same time as the product samples of Table 13, are given in Table 14. By relating the dust concentration given in the table to the total flue gas, a dust loss of approximately 1 per cent was indicated. The fluorine loss in the flue gas was very small, being calculated as only 1.6 per cent. This is verified by the high fluorine content in the product and shows that the process is not dependent upon defluorination.

Table 14. Flue Gas Analyses of Runs IX and X

Run	IX	X
Orsat		
O_2	7.6	8.0
CO_2	6.4	7.8
CO	0.4	1.2
Dust (mg/cu. ft.)	1.0	1.5
Fluorine	11.6	19.6

Pilot Plant Evaluation

The langbeinite-phosphate rock fusion process was demonstrated to be feasible in the pilot plant and a product was obtained containing phosphorus, potassium, and magnesium in an available form. The product had excellent physical characteristics. It was granular, chalk white in appearance when dry and quite soft. The dried product could be stored in open containers without caking.

In general, the equipment and materials of construction used in the pilot plant were satisfactory. The chrome-plastic lining used in the hearth showed practically no corrosion by slag attack and withstood severe abrasion incurred in chipping out the solidified melt between runs. The firebrick in the upper section of the furnace also showed no

corrosion or slag attack. The steel furnace cover and exit flue showed some surface scaling. This appeared to be essentially rust, however, and not an acid attack.

The major problem in the operation of the furnace was tapping the melt. The pilot plant as designed could not be operated successfully with intermittent tapping due to plugging of the tapping outlet, and continuous tapping was necessary. It is believed, however, that enlarging the outlet into a vertical slot instead of a round hole would solve the tapping problem. An auxiliary burner at the tapping outlet would also help the tapping operation in the pilot plant. In a commercial scale plant, tapping would not be as great a problem because of reduced relative heat losses. The relative radiation losses in the hearth would be much less for a large furnace than for the pilot plant and consequently higher hearth temperatures could be expected. Also, the large heat capacity of a commercial scale unit would be an aid in preventing solidification of the melt in the outlet.

Operating data from the pilot plant indicated that approximately 6,000,000 Btu were required per ton of product. As pointed out above, the radiation losses for the pilot plant furnace would be considerably greater than for a commercial plant. Therefore a lower heat requirement per ton could be expected. Using a conservative value of 5,000,000 Btu per ton production cost estimates were made for 20, 50,

and 100 ton per day commercial scale plants proposed for central Iowa. The total manufacturing cost per ton was $40.73, $36.15, and $34.12 per ton, respectively, as shown in Table 15. These estimates were based on 300 days per year operation. The 20 and 40 ton per day plants would have one furnace while the 100 ton per day plant would have two furnaces, each of 50 ton per day capacity. The daily operating schedule was based on 24 hour operation for the furnaces and eight hour operation for the other sections of the plants, except that a 16 hour schedule was assumed for the feed preparation on the 100 ton per day plant. Fixed capital estimates were based on preliminary studies and are probably subject to an error of ±20 per cent.

An indication of the economic feasibility of the various capacity plants is given in Table 16. The selling price was taken as $38.88 per ton to the retailer, based on P_2O_5 and K_2O unit[1] prices of $1.90 and $1.01[2] respectively, with $0.50 per ton premium for granulation. No value has been given to the magnesium content. The selling price would be subject to market acceptance but is probably conservative considering the present market to the farmer of approximately $55.00 for 0-10-15[3] mixed fertilizer. The figures in Table 16 indicate that a 20 ton per day plant would not be economically feasible

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[1] A unit is 20 pounds or 1 per cent of one ton.

[2] From current local process.

[3] Containing 10 per cent P_2O_5 and 15 per cent K_2O.

Table 15. Production Cost Estimate for Fused Langbeinite-Phosphate Plants of Various Capacities

Basis: 1 ton of fused product[a]
300 operating days per year
24 hour per day operation (furnace only)
Location - Central Iowa

	Quantity	Unit Cost	Cost ($) Per Ton of Product		
			20 Ton/day	50 Ton/day	100 Ton/day
Raw Materials[b]					
Langbeinite	0.72 ton	$27.60/ton[d]	$19.88	$19.88	$19.88
Phosphate Rock[c]	0.31 ton	16.40/ton[e]	5.08	5.08	5.08
			$24.96	$24.96	$24.96
Direct Conversion Expense					
Water	1000 gal.	$0.10/M gal	$ 0.10	$ 0.10	$ 0.10
Natural gas	5000 cf	0.25/M cf	1.25	1.25	1.25
Power	24.8 KWH	0.01/KWH	0.25	0.25	0.25
Direct labor[f]		1.50/MH	3.80	2.16	1.44
Maintenance (5% of Fixed Capital/yr.)			1.66	1.13	0.88
			$7.06	$4.89	$3.92
Indirect Conversion Expense					
Depreciation[g] (10% of Fixed Capital/yr.)			$ 3.33	$ 2.26	$ 1.76
Taxes and Insurance (10% of direct labor)			.38	.22	.14
Overhead (50% of direct labor)			1.90	1.08	.72
			$5.61	$3.56	$2.62
Bulk Production Cost			$37.63	$33.41	$31.50
Packaging:					
Bags	25 bags	0.10/bag	$ 2.50	$ 2.50	$ 2.50
Labor			.60	.24	.12
			$3.10	$2.74	$2.62

			$7.06	$4.89	$3.92
Indirect Conversion Expense					
Depreciation[g] (10% of Fixed Capital/yr.)			$ 3.33	$ 2.26	$ 1.76
Taxes and Insurance (10% of direct labor)			.38	.22	.14
Overhead (50% of direct labor)			1.90	1.08	.72
			$5.61	$3.56	$2.62
Bulk Production Cost			$37.63	$33.41	$31.50
Packaging:					
Bags	25 bags	0.10/bag	$ 2.50	$ 2.50	$ 2.50
Labor			.60	.24	.12
			$3.10	$2.74	$2.62
Total Production Cost			$40.73	$36.15	$34.12

[a]Analysis: 13.3% P_2O_5, 13.0% K_2O, 11.5% MgO.

[b]Assuming a 1% dust loss and 2% handling loss.

[c]32.5% P_2O_5.

[d]Including $11.60/ton freight to Ames, Iowa.

[e]Including $10.60/ton freight to Ames, Iowa.

[f]2.40, 1.44, and 0.96 man hours/ton estimated for the 20, 50, and 100 ton per day plants, respectively.

[g]$200,000, $340,000, and $525,000 fixed capital cost estimated for the 20, 50, and 100 ton per day plants, respectively.

Table 16. Estimated Return on Investment for Fused Langbeinite-Phosphate Plants of Various Capacities

	20 ton/day	50 ton/day	100 ton/day
Annual Sales, tons	6,000	15,000	30,000
Annual Sales, dollars[a]	$233,000	$583,000	$1,166,000
Annual Total Prod. Cost	244,000	542,000	1,023,000
Gross Profit	-$11,000	$41,000	$143,000
Selling and Admin. Expense (5% of total sales)	11,650	29,150	58,300
Net Profit	-$22,650	$11,850	$84,700
Income Tax (50%)[b]	0	5,930	42,350
New Earnings	-$22,650	$5,920	$42,350
Return on Fixed Capital, %	loss	1.7	8.1
Return on Fixed plus Working Capital,[c] %	loss	1.3	5.5

[a]Assuming a selling price of $38.88.

[b]Estimated for 1952 corporate taxes.

[c]Estimated as $49,320, $122,500, and $244,300 for the 20, 50, and 100 ton per day plants, respectively.

and that the "break even" capacity is about 50 ton per day. A higher selling price could probably be expected locally and this would directly increase the return. The annual production from a 100 ton per day plant would represent only about 10 per cent of the 1951 fertilizer consumption of Iowa alone.

Because of the magnesium content, the fused langbeinite-phosphate would be especially adapted to soils with magnesium deficiencies. This is generally true of the Atlantic and Gulf Coastal Plains soils. In areas where there is high rainfall, considerable loss of magnesium occurs by leaching, leaving the soil deficient in magnesium. Many growing crops, such as alfalfa, soybeans, clover hay, tobacco and cotton require large amounts of magnesium which must be added as fertilizer in the same way as phosphorus and potassium.

For these regions, the langbeinite-phosphate product would probably market at a higher price than $38.88 per ton used for the figures in Table 16. Since the production costs would be essentially the same, except for freight rates, the process would be definitely favorable economically.

CONCLUSIONS

1. The P_2O_5 in rock phosphate can be made available by fusion of the phosphate with magnesium sulfate or mixtures of magnesium sulfate and potassium sulfate and immediately quenching in a suitable medium, without substantial removal of the fluorine present in the rock phosphate.

2. Three component fusion studies of phosphate rock, magnesium sulfate, and potassium sulfate indicate that compositions within the shaded area of Figure 14 are necessary to obtain fusion products of high P_2O_5 availability.

3. Langbeinite ($K_2SO_4.2MgSO_4$) can be used instead of the pure components in fusions with phosphate rock to obtain a product of high P_2O_5 availability. The data indicate that a minimum proportion of seven parts of langbeinite to three parts of phosphate rock is necessary to obtain a fused product having a P_2O_5 availability of 95 per cent or greater.

4. Fusion of a mixture of seven parts of langbeinite and three parts of phosphate rock, containing 32.5 per cent P_2O_5, gave a product containing 15.6 per cent total P_2O_5, 11.9 per cent MgO, 11.6 per cent K_2O, and 1.6 per cent F. The availability of the phosphorus and magnesium was 97 per cent and the availability of potassium was 95 per cent. The

product had excellent physical characteristics. It was chalk white, easily ground, and not hygroscopic.

5. Melting point studies showed that mixtures of langbeinite and phosphate rock containing a minimum of 70 per cent langbeinite melted at approximately a constant temperature of 1600° F. The melting point of mixture containing less than 70 per cent langbeinite increased rapidly as the proportion of phosphate rock increased.

6. Tungsten crucibles were satisfactory for the laboratory fusions for all compositions of langbeinite and phosphate rock mixtures. Porcelain crucibles were satisfactory for fusions of compositions containing more than 50 per cent langbeinite since the temperatures required in this range were much lower.

7. Pilot plant studies indicate that the langbeinite phosphate rock fusion process can be carried out on a large scale in a vertical shaft kiln, using natural gas as a fuel.

8. The pilot plant operated successfully using continuous tapping and could be run continuously at a production rate of 100-150 pounds of product per hour. The product was finely granulated by the quenching sprays and P_2O_5 availabilities as high as 95 per cent were obtained.

9. The chrome plastic hearth lining was satisfactory under furnace operating conditions and showed no corrosion or slag attack. The lining also withstood considerable

abrasion due to chipping of solidified melt from the hearth.

10. Production costs were estimated to be $40.73, $36.15, and $34.12 per ton of fused product for a 20, 50, and 100 ton per day plant, respectively. With an assumed selling price of $38.88 per ton, calculations indicated that the "break-even" capacity was approximately 50 tons per day and that a 100 ton per day plant would have a return on the total investment of 5.5 per cent.

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A P P E N D I X

APPENDIX A

Preparation of Tungsten Crucibles

Materials used

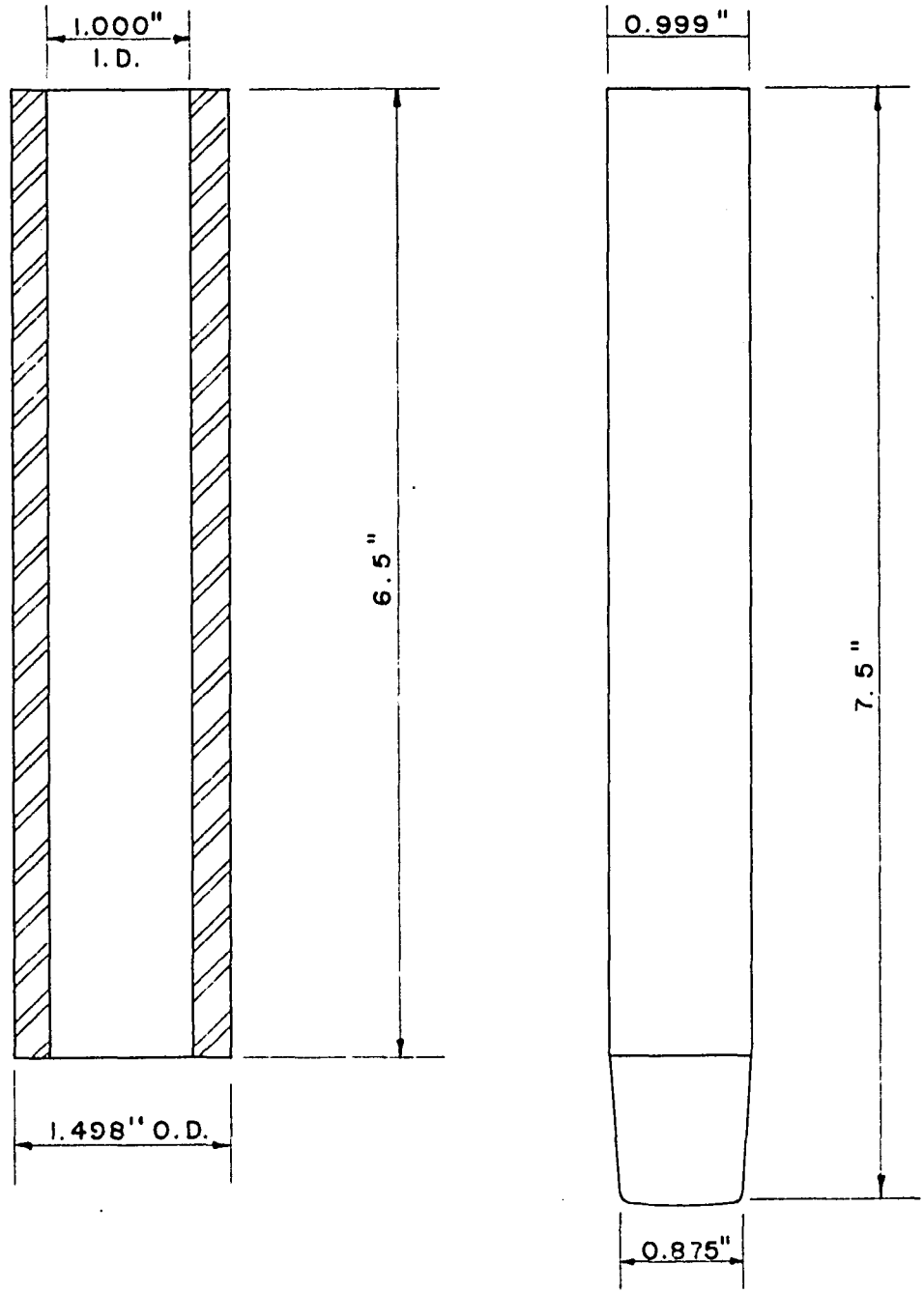
1. Tungsten powder - Fansteel type 427 (200 mesh).
2. Carbowax.
3. Steel die (C = 1.05%, Mn = 0.20, Si = 0.20) as shown in Figure 28.

Procedure

The steel die was machined oversized and heat treated as follows: The pieces were separately heated to 790-800° C., held for 15 minutes, quenched in water, and drawn for one hour at 200° C. The cylinder and rod were then ground to exact dimensions as shown in Figure 28.

One-half teaspoon of Carbowax was mixed with water and several drops of the solution added to about 400 grams of the tungsten powder. About 150 grams of the tungsten powder were loaded into the die and pressed at 10,000 psi. Then the remainder was added and pressed at 50,000-60,000 psi, in stages, intermittently releasing the pressure. The final pressure was retained for 10-15 minutes.

The formed crucible was removed from the die, placed in a graphite holder and put in an electric resistance furnace. The furnace was evacuated to 10 μ and held overnight. It was then heated to 800° C. over a period of three hours and allowed to cool in the furnace under vacuum. The crucible was then sintered in an Ajax high frequency induction furnace at 2000-2100° C. for 15 minutes under vacuum. The furnace was then shut off and the crucible allowed to cool. Pressures in the furnace were 40 μ at the start, 200 μ at maximum and 15 μ after cooling.



ALL TOLERANCES PLUS 0.000", MINUS 0.001"

Figure 28. Detail Drawing of Crucible Die.

APPENDIX B

X-Ray Studies of the Langbeinite-Phosphate Product

X-ray powder patterns were taken of typical langbeinite-phosphate rock fusion products by a Norelco Geiger Counter X-ray Spectrometer[1] consisting of the basic diffraction unit, high angle precision geiger counter goniometer, electronic circuit panel and automatic strip recorder. The assembled apparatus is shown in Figure 29.

Powder patterns for fusions 47-1 and 47-2 are shown in Figure 30. The horizontal axis is the "two theta angle" (2θ) which is numerically equal to twice the angle made by the specimen plane and the main beam. The fusions were made from a mixture containing 70 per cent langbeinite "A" and 30 per cent phosphate rock. Fusion 47-1 was quenched in air. Fusion 47-2 was quenched in water. The P_2O_5 availabilities were 79 per cent and 100 per cent respectively. The figure shows that fusion 47-1 has stronger crystalline lattices than fusion 47-2.

Figure 31 shows a slow speed pattern for fusion 47-1 compared to patterns for the phosphate rock and langbeinite

[1] In the Ames Laboratory of the Atomic Energy Commission, Ames, Iowa.

used. A nickel foil filter was used for the patterns shown in Figure 31 to minimize background reflections. Qualitatively, the comparison of raw material and product patterns in Figure 31 shows that certain well defined crystalline lattices of the rock are greatly reduced or entirely eliminated in the product. This is especially true of the peak in the phosphate rock pattern at an angle of reflection of 32.1 (2θ). The enlargement of the area under the peaks in the product pattern as well as the indistinct diffraction line indicates a transition to an amorphorus structure. These observations, however, are insufficient to state definitely that the product is a glass.

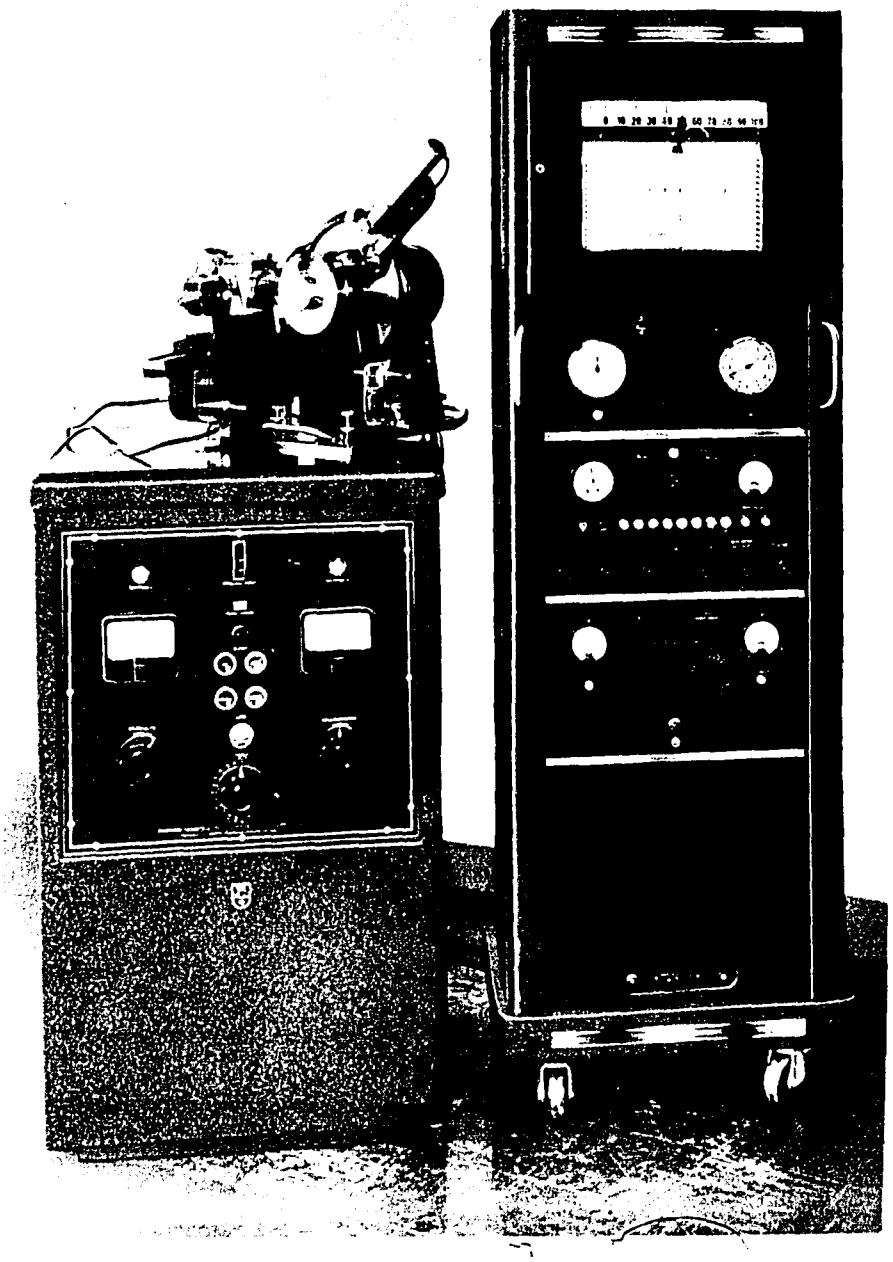


Figure 29. Norelco Geiger Counter X-ray Spectrometer.

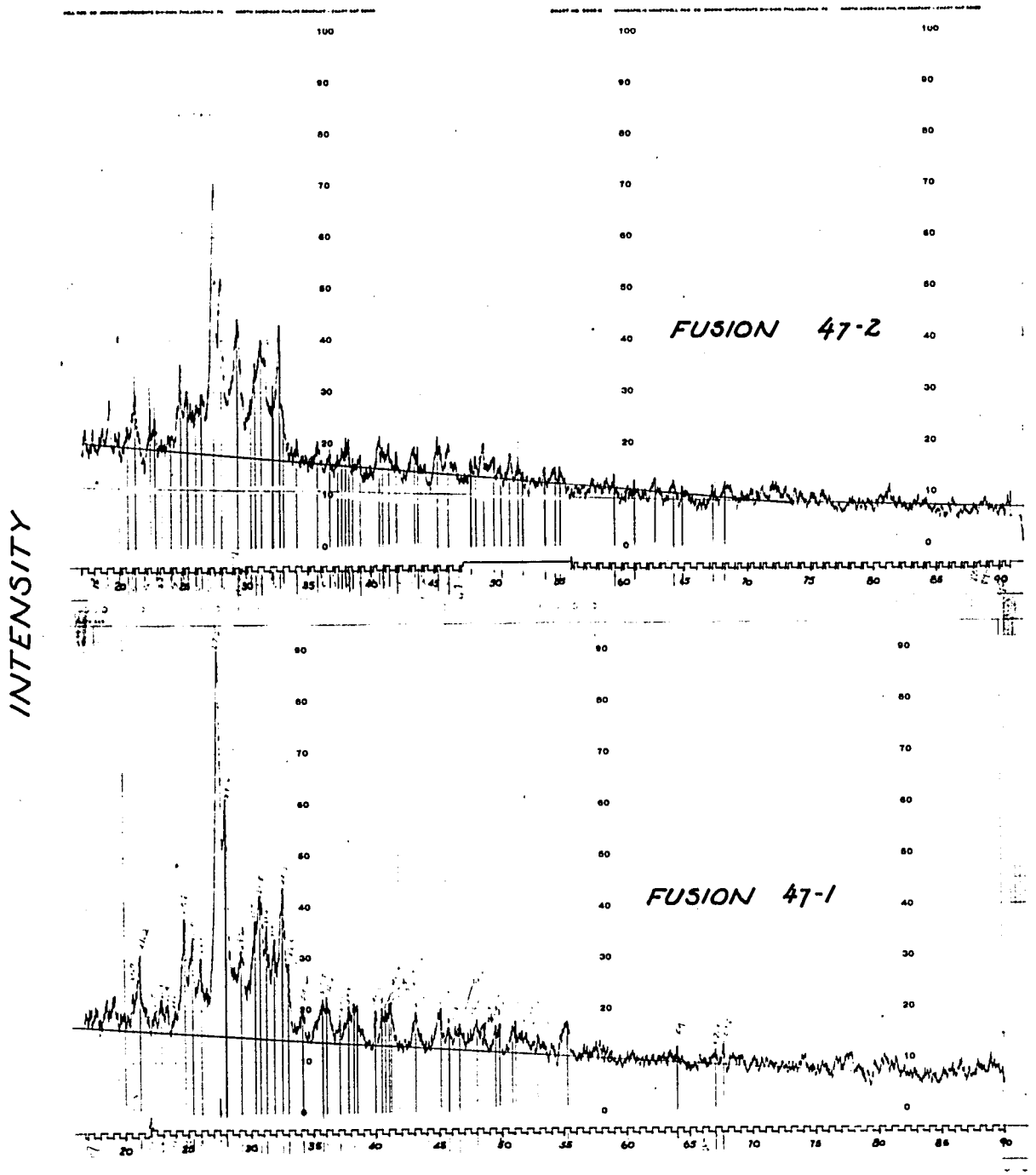
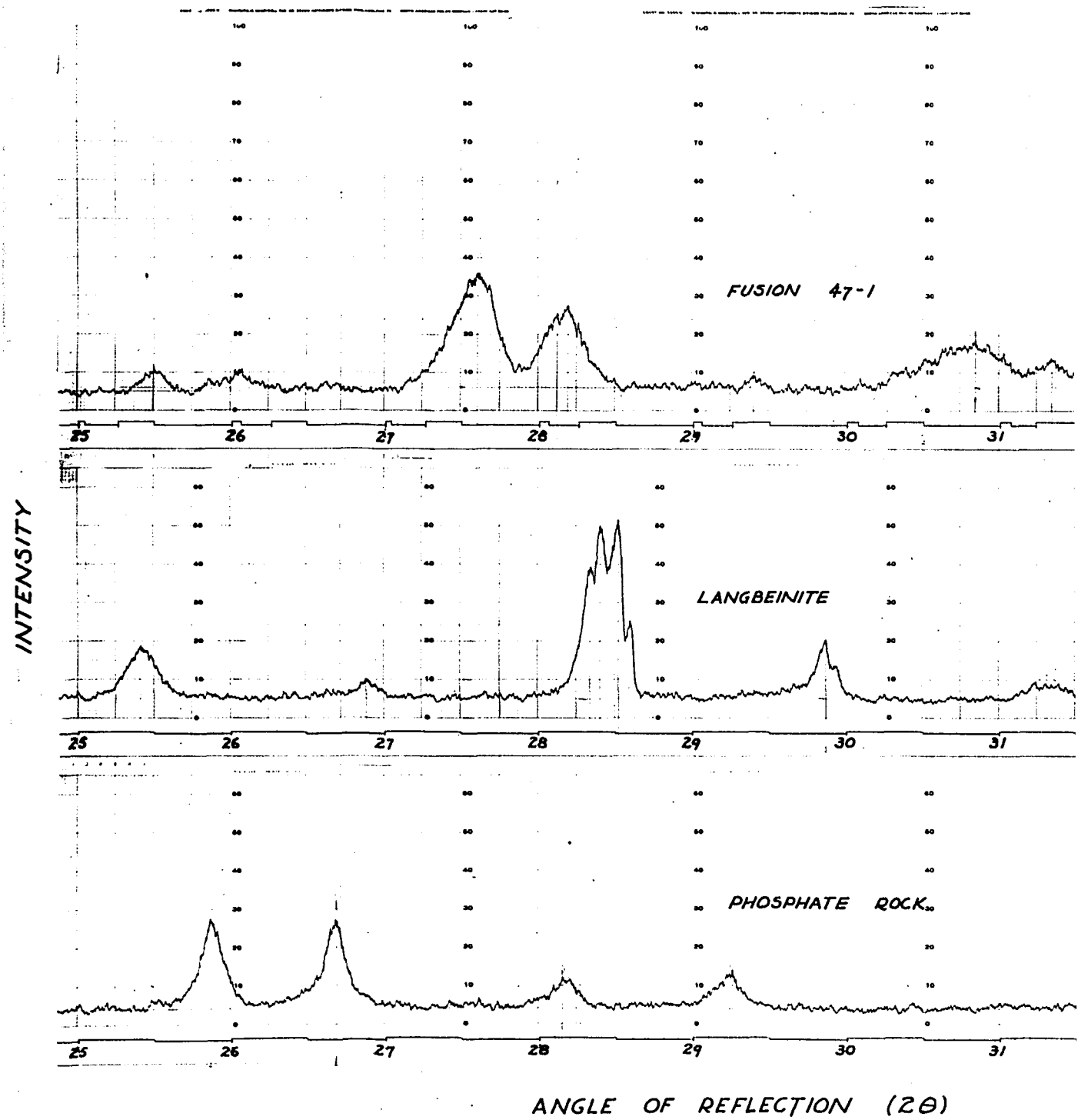
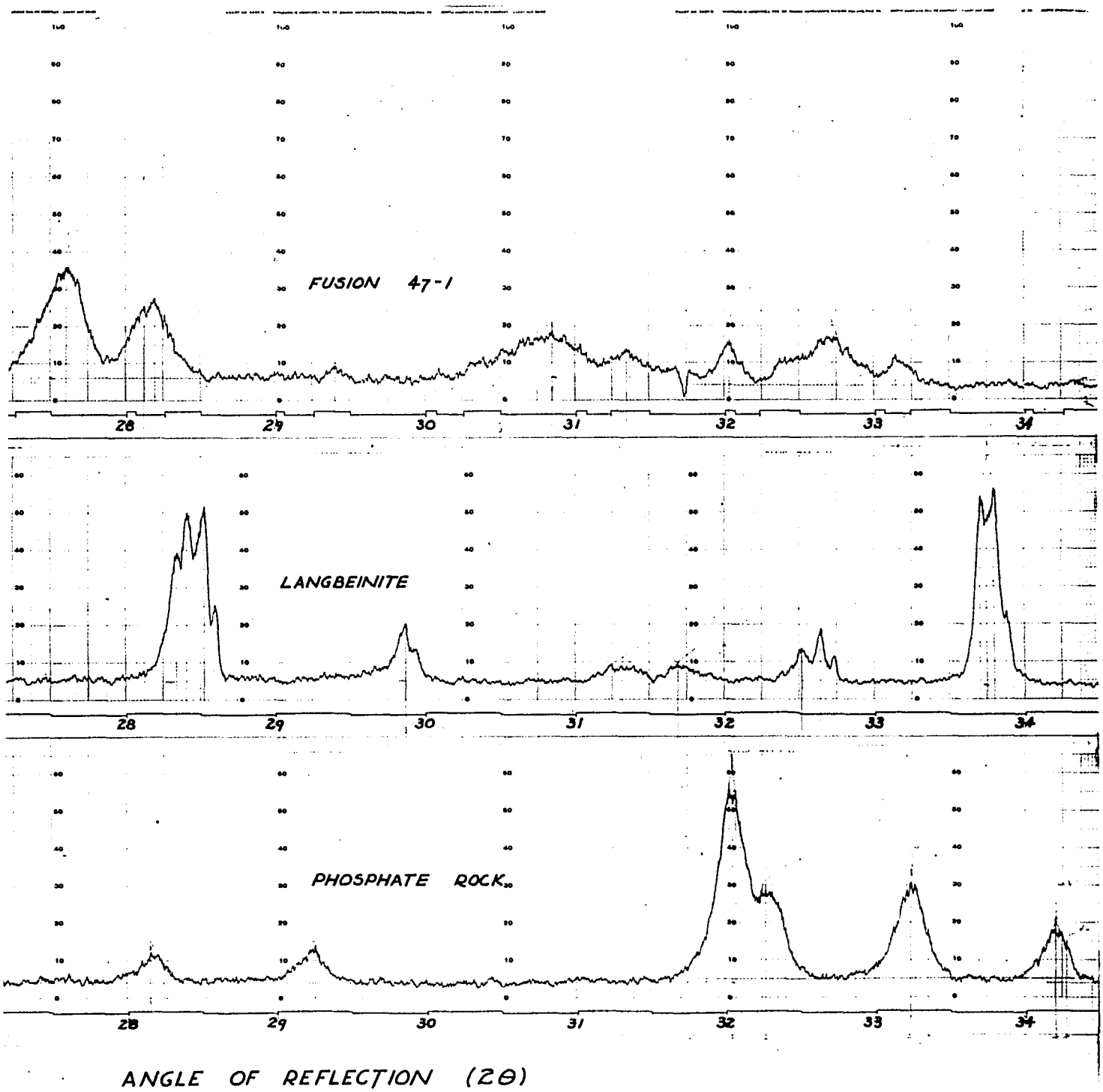

FUSION 47-2
FUSION 47-1
INTENSITY
ANGLE OF REFLECTION (2θ)

Figure 31. Comparison of X-ray Diffraction Patterns of Langbeinite-Phosphate Raw Materials and Fused Product Obtained with Copper K Radiation (Time Constant 8, Scale Factor 2, Nickel Foil Filter).


FUSION 47-1
LANGBEINITE
PHOSPHATE ROCK
INTENSITY
25
26
27
28
29
30
31
ANGLE OF REFLECTION (2θ)


FUSION 47-1
LANGBEINITE
PHOSPHATE ROCK
28
29
30
31
32
33
34
ANGLE OF REFLECTION (2θ)